Eletrochemistry
FB (obj)

① Ⓓ Theory

② Ⓑ "

③ Ⓓ "

④ B

⑤ As salt bridge is removed the circuit will become open so $E = 0$ Ⓐ

⑥ e^- travel from anode to cathode

Ⓑ

⑦ Ⓑ

⑧ Ⓑ

⑨ Ⓒ Calomel electrode is also used as reference ~~elect~~ electrode.

⑩ Ⓓ

11 D Check

12 B Cu can disblace silver from i'ts salts

13 C Zinc has higher oxidation potential than H_2

14 D Theory

15 A A has highest magnitude of electrode potential so most active

16 A For strongest reducing agent oxidation potential should be highest.

17 A

18 D Copper is lesser active than Iron

⑲ Ⓑ Iron is more active metal than copper.

⑳ Ⓐ Hg ~~has~~ cannot displace Hydrogen

㉑ Ⓐ Cu being more active metal than silver displaces it from its salt and blue colour is due to hydrated copper ions

㉒ Ⓓ Since Al is more active metal than Cu

㉓ $E^0_{B^{2+}|B} - E^0_{A^{2+}|A} > 0$

so. A will dissolve and B will be deposited of A

Ⓑ

㉔ Ⓑ Zn has a +ve tendency of oxidation so it is a reducing agent

㉕ -ve reduction potential means +ve oxidation potential

so A^- is readily oxidised

㉖ Al being more active metal than Cu will displace it from its salt so Al will be oxidised

Ⓒ

㉗ $E^0_{cell} = E^0_{Ag^+|Ag} - E^0_{Sn^{2+}|Sn}$

$= 0.8 - -0.14 = 0.94$ (D

㉘ Ⓑ

㉙ 0.799 ⇒ cathode

−0.44 ⇒ anode.

Ⓐ

㉚ $E^0_{cell} = E^0_{O_2|H_2O|OH^-} - E^0_{Fe^{2+}|Fe}$

$= 0.4 - - 0.44 = 0.84$ V

Ⓒ

㉛ $E^0_{cell} = E^0_{Fe^{2+}|Fe} - E^0_{Zn^{2+}|Zn}$

$= -0.41 + 0.76$

$= 0.35$ V Ⓑ

(32) ~~E^0_{cell} FS n~~

~~Bo~~ (ii) & (iii) (A)

(33) $E^0_{cell} = 0.14$

$K = 10^{\frac{2\times 0.14}{0.059}} = 5.5\times10^4$ (A)

(34) Since reduction potential of Sn^{2+} is higher.

So $3Sn^{2+} + 2Cr \longrightarrow 3Sn + 2Cr^{3+}$

(C)

(35) (A)

(36) $E^0_{cell} = -0.14 - -0.74 = 0.6$

(C)

(37)

$K = 10^{\frac{6\times 0.6}{0.059}}$ (D)

㊳ $\Delta G^\circ = -RT\ln K = -nFE^\circ$

$= -347.4$ kJ Ⓓ

㊴ For feasible rxn $\Delta G < 0$

$\Rightarrow K > 1$ Ⓓ

㊵ $E^\circ_{Fe^{3+}|Fe} = \frac{0.77\times 1 - 0.44\times 2}{3}$

$= -0.0367$

Ⓒ

㊶ Ⓐ

㊷ $E_{cell} = 1.1 - \frac{0.059}{2}\log\frac{0.1}{0.1}$

$= 1.1$ Ⓐ

㊸ $E_{cell} = 0.12 - \frac{0.059}{2}\log\frac{1}{(3.5)(1.7)^2}$

(44)

$$E^{o}_{cell} = 0.96 - 0.799$$
$$= 0.161$$

$$E_{cell} = 0.161 - \frac{0.059}{3} \log \frac{0.2 \times (0.01)^3}{2 \times (0.1)^4}$$

$$= 0.22\ V.$$

(C)

(45)

$$E^{o} = 0.1 + \frac{0.0592}{2} \log K_{sp}$$
$$= 0.1 - \frac{0.0592}{2} \log \frac{1}{K_{sp}}$$

(B)

(46)

$$E^{o}_{cell} = 0.799$$

$$E_{cell} = 1.05 = 0.799 - \frac{0.059}{1} \log \frac{[H^+]}{0.1}$$

$$[H^+] = 5.5688 \times 10^{-6}$$

$$pH = 5.254$$

(B)

㊼

$$0.071 = 0.8 + \frac{0.059}{1}\log K_{sp}$$

$$K_{sp} = 4.4 \times 10^{-13}$$

㊽ Ⓒ

㊾

$$E^{o}_{cell} = -0.45 - -1.66$$

$$= 1.21V$$

$$E_{cell} = 1.21 - \frac{0.059}{6}\log\frac{(0.1)^2}{(0.02)^3}$$

㊿

$$= 1.1795\ V.$$

$$E_{Zn|Zn^{2+}} = E^{\ominus}_{Zn|Zn^{2+}} - \frac{0.059}{2}\log[Zn^{2+}]$$

$[Zn^{2+}]$ decrease by factor of 10

So change $= -\,0.059 \log \frac{1}{\ }$

(51) (B)

(52) $E_{cell} = -\frac{0.059}{2}\log\frac{[Fe^{2+}]_{anode}}{[Fe^{2+}]_{cathode}}$

For spontaneous $E_{cell} > 0$

so $[Fe^{2+}]_a < [Fe^{2+}]_{cath.}$

net reaction $Fe^{2+}(1m) \rightarrow Fe^{2+}(0.1m)$

so (B)

(53) $E_{cell} = -\frac{0.059}{1}\log\frac{0.001}{1}$

so (C)

(54) $0.648 = -0.059\log\frac{K_{sp}}{0.1 \times 0.1}$

$K_{sp} = 1.26 \times 10^{-13}$

(55)

$$E_{cell} = -\frac{0.059}{2}\log\frac{0.05}{1.5}$$

$= 0.0434\ V.$ (C)

(56)

$$\frac{dE_{cell}}{dT} > 0$$

As cell discharges E_{cell} decreases

so $dE_{cell} < 0$

$\Rightarrow dT < 0$ $\Rightarrow$ (B)

(57)

~~$0.67 = 0.28 - 0.059 \log [H^+]$~~

~~$\Rightarrow pH = \frac{0.67 - 0.28}{0.059}$~~

~~$= 6.6$~~ (A)

(58) $-0.365 = -0.126 + \frac{0.059}{2} \log K_{sp}$

$K_{sp} = 8.9 \times 10^{-9}$

Ⓓ

(59) $\frac{dE^\circ}{dT} = -0.00017$

$\Delta H^\circ = -2 \times 96500 \times 1.058 - 298 \times 2 \times 96500 \times 0.00017$

$= -213{,}97 \text{ kJ}$

Ⓓ

(60) $E_{cell} = E^\circ_{cell} - 0.059 \log[H^+]$

$E_{cell} = E^\circ_{cell} + 0.059\, pH$

Ⓑ

Electrolysis

(61) As per theory (A)

(62) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ cathode

$2Cl^- \rightarrow Cl_2 + 2e^-$ anode.

Ans - (A)

=

(63)

Cathode. $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

$\Rightarrow$ (A)

(64) Same as (62) (B)

(65) (D) reduction occurs at cathode

(66). (C)

(67) anode:- $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

(C)

(68) $Cu \rightarrow Cu^{2+} + 2e^-$ (D)

active metal as anode

(69) Ⓑ overvoltage of H_2 liberation on Hg is high

(70) Ⓑ

Faraday's law

(71) F (charge required) $\rightarrow$ for E gm of Na

$$E = \frac{23}{1} = 23 \text{ gm}$$

for 11.5 gm $\Rightarrow$ 0.5 F charge will be required

(72) Faraday

(73) Resistance, as $m \propto i\,t\,E$

(74) Chemical equivalents

(75) $E = \frac{m}{Q} = $ gm/coulomb

(76) 1 Faraday = 96500 Coulombs

(77) Faraday (as per theory)

(78) NaCl, as 1 gm atom = 1 gm equivalent

(79) $(n_E)_{H_2} = (n_E)_{Cu}$ [for same Q]

$$\frac{0.504}{1} = \frac{m}{31.75}$$

$$m \simeq 15.9 \text{ gm}$$

(80) At anode

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

At cathode

~~81~~ for 1 mole of O_2 we will get 4 mole of Ag

for 1.6 gm $\Rightarrow \frac{1.6}{32} \times 4$ moles of Ag

$\Rightarrow$ 0.2 moles of Ag

$\Rightarrow 0.2 \times 108$

$=$ 21.6 gm of Ag

(81) $\frac{m_1}{m_2} = \frac{E_1}{E_2}$ (for same charge)

$m_1 = 19.5 \times \frac{9}{39} = 4.5$ gm

(82) 112 ml $\rightarrow \frac{112}{22400} =$ ~~0~~5×10^{-3} moles

$m = z i t$

$m = \frac{E}{F} i t \Rightarrow i = \frac{mF}{E t}$

$\Rightarrow \frac{5 \times 10^{-3} \times 2 \times 96500}{965 \times 1} = 1$ A

(83) ~~A~~ silve nitrate

(84) $Q = It = 100 \times 10^{-3} \times 30 \times 60$

$= 180$ C

(85) $m = Z I t$

$m = \frac{E}{F} I t \Rightarrow E = \frac{m \times F}{It}$

(86). It holds for all temp.

(87) equivalent weight of the electrolyte

(88) As per theory

(89) 1 mole $\simeq 6\times10^{23}$

(90) 1 faraday

(91) $\frac{9650}{F} = 0.1$ Faraday

0.1 E mass will be deposited

i.e. 10.8 gm

(92) 3 Faraday will transfer 3 moles of e^-

& neutralized 1.5 mole Fe^{2+}

$\Rightarrow 1.5\times56$ gm

$=$ 84 gm

(93) $m = \frac{E}{F} it = \frac{63.5}{2\times96500}\times386\times25$

$=$ 0.3175 gm

(94) $\frac{m_1}{m_2} = \frac{E_1}{E_2} \Rightarrow m_1 = 1.08\times\frac{63.5/2}{108}$

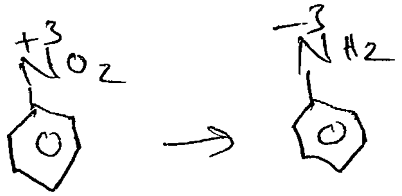
$=$ 0.3177 gm

(95) Al^{3+} ⇒ 1 gm atom will required 3 mole of electron

(97) 4 gm equivalents will required 4 Faraday

(98) 12.3 gm ⇒ $\frac{12.3}{123}$ moles

⇒ 0.1 moles



N - factor = 6

0.6 Faraday charge will be required

= 57900 C

(99) 1 gm atom ≡ 2 equivalents

= 2F charge

1 gm Mg → 5 Rs (n - factor = 2)

Al ⇒ n - factor = 3

1 gm Al → $5 \times 3/2$ = 7.5 Rs

10 gm Al → 75 Rs

(100) 1 gm Mg ⇒ $\frac{1}{12}$ equivalents

10 gm Al ⇒ $\frac{10}{9}$ equivalents

charge = $5 \times \left(\frac{12}{1}\right) \times \left(\frac{10}{9}\right)$ = 66.67 Rs

(10[illegible]). 0.1 Faraday → 0.1 equivalent

$\Rightarrow 0.1 \times 9$ gm

(102) 6×10^{20} electrons $= \frac{6 \times 10^{20}}{6 \times 10^{23}} = 10^{-3}$ moles

$\simeq 0.001$ equivalents

(103) $Al^{3+} : Cu^{2+} : Na^{+}$

$1 : 1.5 : 3$

(104) Total volume $= 0.25 \times 2 \times 10^{-5}\ m^3$

mass = density × volume

$= 0.25 \times 2 \times 10^{-5} \times 7190$ kg

$= 0.03595$ kg

$= 35.95$ gm

$$m = \frac{E}{F} It$$

$$t = \frac{35.95 \times 96500}{8.67 \times 75} = 5335 \text{ sec}$$

$\simeq 1.5$ hr

[illegible]

(96) ~~2.15~~ $m = \frac{E}{F} It$

$$t = \frac{2.19 \times 96500}{(52/3) \times 35.2} = 346 \text{ Sec}$$

$= 5.77$ min.

Conductance

(105). As per theory

(106) number of ions

(107) sulphuric acid, As its easily dissociates into ions

(108) HCl, A it will easily dissociate

(109) Graphite, having ~~two~~ 1 free electron on each carbon

(110) As per theory

(111) As per theory

(112) As per theory

(113) As per theory

(114) molar conductivity = $\Omega^{-1} cm^{2} mol^{-1}$

(115) 0.001 M (as it has minimum conc.)

(116) As per theory

(117) cell constant = $\frac{l}{A} = \frac{2.5}{5} = 0.5$

(118) As difluoroacitic acid is strongest electrolyte

(119) As per theory

(120). As per theory (~~[illegible]~~

(121) Electrolyte can be weak also at infinite dilution

(122) ~~l~~l/A ↗ depends only on dimension
(l/A = cellconstan)

(123) $\lambda_m^\infty(CH_3COOH) = \lambda_m^\infty(CH_3COO^-) + \lambda_m^\infty(H^+)$

$= \lambda_m^\infty(HCl) + \lambda_m^\infty(CH_3COOK) - \lambda_m^\infty(KCl)$

$= 269.12\ S\,cm^2\,mol^{-1}$

(124) for 1% ionized $= 19\ S\,cm^2\,mol^{-1}$

for 100% ionized $= 1900\ S\,cm^2\,mol^{-1}$

Get Eq

① 1 F of electricity liberates one gm. eq.

For NaCl 1 gm eq = 1 gm mole

⇒ (A)

② with Hg cathode Na will form amalgam, due to high overvoltage of H_2 liberation.

③ 108g Ag = $\frac{108}{108}$ mole Ag = 1 eq Ag.

⇒ electricity reqd = 1 F.

④ $E^{0}_{Fe^{3+}|Fe^{2+}} = \dfrac{(-0.036\times3) - (2\times-0.44)}{1}$

$= 0.772.$

⑤ From Electrochemical series.

$Y > Z > X.$

⑥

$\Lambda_{CH_3COOH} = 91 + 426.16 - 126.45$

$= 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

⑦ $0.0112 = \frac{1}{55} \times \left(\frac{l}{A}\right) \Rightarrow \frac{l}{A} = 0.616 \text{ cm}^{-1}.$

⑧ Ⓑ

⑨ Ⓑ

⑩ $w = 108 \times \frac{9.65}{96500} = 10.8 \times 10^{-3} g \Rightarrow$ Ⓒ

⑪ $9 = 9 \times \frac{Q}{96500} \Rightarrow Q = 96500 C$

$\Rightarrow$ Ⓑ

⑫ At cathode reduction occurs

so Ⓐ is not possible at cathode.

⑬ Ⓓ

⑭ metal used for galvanization should

(15)

~~$\Lambda^{\infty}_{e, BaSO_4}$~~

$$\Lambda^{\infty}_{m, BaCl_2} = 2x_1$$

$$\Lambda^{\infty}_{m, H_2SO_4} = 2x_2$$

$$\Lambda^{\infty}_{m, HCl} = X_3$$

$$\Rightarrow \Lambda^{\infty}_{m, BaSO_4} = 2x_1 + 2x_2 - 2x_3$$

So $2(x_1 + x_2 - x_3) = y \times \frac{1000}{S}$

$$\Rightarrow S = \frac{10^3 y}{2(x_1 + x_2 - x_3)}$$

$$\Rightarrow K_{sp} = S^2 = \frac{10^6 y^2}{4(X_1 + X_2 - X_3)^2}$$

(16) (D)

Before end pt. H^+ ions are replaced by Na^+ so conductane decreases slightly. After end pt. OH^- ions ~~are~~ increases conductance.

(17)

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{c\left(\frac{\Lambda_m}{\Lambda_m^\infty}\right)^2}{1-\frac{\Lambda_m}{\Lambda_m^\infty}}$$

$$K_a = \frac{c\Lambda_m^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m)} \Rightarrow (B.)$$

(18)

$$\frac{8.7}{87} = n_{e^-} = 0.1$$

$$\Rightarrow 4.825 \times 10^{-3} \times t = 0.1 \times 96500$$

$$t = 2 \times 10^6 \text{ sec} \quad (A.)$$

(19)

$$E_1 = 0.0591\, pH_1 \;;\; pH_1 = pK_a + \log \frac{x}{y}$$

$$E_2 = 0.0591\, pH_2 \;;\; pH_2 = pK_a + \log \frac{y}{x}$$

$$\Rightarrow E_1 + E_2 = 0.0591(2pK_a)$$

$$pK_a = \frac{E_1 + E_2}{0.118} \Rightarrow (A.)$$

(20)

$$E_1 = E^0$$

$E \quad E^0 \quad 0.0591$ so (D.)

(21) (A) (B) (C)

As pe theory.

(22) $\Delta G \neq 0$

Net reaction $Fe^{2+}(0.1\ M) \rightarrow Fe^{2+}(0.01M)$

so (B) & (C)

(23) (B), (D)

(24)

$$E_{cell} = E^{0}_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]\, p_{H_2}}{[H^+]^2}$$

where $E^{0}_{cell} = 0.76$

So. (A), (B) (D)

(25)

$$\begin{tikzcd} BrO_4^- & BrO_3^- \arrow[l, "-1.74V"'] & HOBr \arrow[l, "-1.47"'] \arrow[ll, bend left, "-1.56"] \arrow[r, "1.6V"] \arrow[rr, bend right, "1.335V"'] & \frac{1}{2}Br_2 \arrow[r, "1.07V"] & Br^- \end{tikzcd}$$

So possible products Br_2, BrO_3^-

& Br_2, BrO_4^-

(B), (C)

㉖

$$E_{cell} = -\frac{0.0591}{2}\log\frac{x_1^2\ P_2}{x_2^2\ P_1}$$

so For $E_{cell} > 0$

$x_1 < x_2$ if $P_1 = P_2$ Ⓑ

$P_2 < P_1$ if $x_1 = x_2$. Ⓒ

㉗

~~so~~ $Z_2 + 2X^- \longrightarrow X_2 + 2Z^-$ spontaneer

$Z_2 + 2Y^- \longrightarrow Y_2 + 2Z^-$ non-spontan

so. $E^\circ_Z - E^\circ_X > 0$

& $E^\circ_Z - E^\circ_Y < 0$

Ⓐ, Ⓒ

㉘ Ⓐ Ⓓ

㉙ A, B, D,

㉚

$$(62.3+67.7) = 3.4\times10^{-6}\times\frac{1000}{S}$$

$$\Rightarrow S = 2.6\times10^{-5}\ \text{mol/Lt}$$

$$= 3.75\times10^{-3}\ \text{g/Lt.}$$

Ⓐ , Ⓑ

㉛ Ⓐ Ⓓ

㉜ Ⓐ Ⓑ

㉝ $$n_e = \frac{2.68\times3600}{96500}$$

$$wt_{Cu} = \frac{n_e}{2}\times63.5 = 3.174\ \text{g.}$$

Ⓐ , Ⓑ ,

㉞

[illegible] —

~~$Ag \rightarrow Ag^+ + e^-$ E_1^0~~

~~$AgI + e^- \rightarrow Ag + I^-$ E_2^0~~

㉞

E

~~$Ag^+ + e^- \rightarrow Ag \quad E_1^0 \rightarrow K = 10$~~

$AgI \rightarrow$ ~~Ag^+~~ $+ I^- \quad 10 \quad K_{sp}$

㉞

$$E^0_{I^-|AgI|Ag} = E^0_{Ag^+|Ag} + \frac{2.303RT}{nF} \log K_{sp}$$

Given $E^0 = E^0_{I^-|AgI|Ag} - E^0_{Ag^+|Ag}$

$$\Rightarrow E^0 = \frac{2.303RT}{nF} \log K_{sp}$$

$\Rightarrow$ Ⓓ

㉟

$$\Delta H = -nF\left[E - T\left(\frac{dE}{dT}\right)_p\right]$$

$$= -2 \times 96500\left(0.6753 - 298 \times \frac{0.6753 - 0.6915}{15}\right)$$

$$= -192.45 \text{ kJ.}$$

㊱ $n_{e^-} = \frac{4 \times 3600}{96000} = 0.15$

For $Fe^{3+} \rightarrow Fe^{2+}$, n_{e^-} reqd $= 0.1$
(0.1 mole)

so $2e^{-} + 1Fe^{2+} \longrightarrow Fe$

$n_{Fe} = \frac{0.05}{2} = 0.025$

so Ⓐ Ⓑ , Ⓒ

㊲ B

㊳ Ⓐ Ⓓ

㊴ if $E^{\circ}_{M^{n+}|M} < 0$

so $E^{\circ}_{H^{+}|H_2} - E^{\circ}_{M^{n+}|M} > 0$

so Ⓐ

if $E^{\circ}_{M^{n+}|M} > 0$

so $E^{\circ}_{M^{n+}|M} - E^{\circ}_{H^{+}|H_2} > 0$

so Ⓑ

if $E^{\circ}_{M^{n+}|M} > 0$ ⇒ cathode

⇒ $\boxed{+ve}$ electrode

(42) (A) (C)

(43) $$E = -\frac{0.0592}{2}\log\frac{[Pb^{2+}]_{anode}}{[Pb^{2+}]_{cathode}}$$

(so) (A) (C)

$$\because\ [Pb^{2+}]_{anode} = \sqrt{K_{sp}(PbSO_4)}$$

$$[Pb^{2+}]_{cathode} = \sqrt[3]{\frac{K_{sp}(PbI_2)}{4}}$$

(44) $$E_{cell} = E^{\circ}_{cell} \pm \frac{0.0591}{2}\log\frac{[Cd^{2+}]}{[Cu^{2+}]}$$

so for increasing Ecell

$[Cd^{2+}]\downarrow$ & $[Cu^{2+}]\uparrow$.

(B), (C),

Passage 1

① $E = \dfrac{827 \times 10^3}{4 \times 96500} = 2.14\ V.$ Ⓐ

② $K_c = Q$ at - eq.

Hence $E_{cell} = 0$ Ⓒ

③ $E^0 = \dfrac{0.0592}{n} \log K$

$\Rightarrow Y = kx. \Rightarrow$ Ⓐ

④ $K_c =$ ~~ad~~ $\text{antilog}\left(\dfrac{0.46 \times 2}{0.0591}\right)$ Ⓐ

$K_c = \text{antilog}(15.57)$

⑤ $K_c = 10^{\frac{1.1 \times 2}{0.0591}} \simeq 10^{37}$ Ⓑ

② Passage - 2

① Ⓒ

② Ⓑ

③ $K = \sigma \times \frac{l}{A}$

given $K = \sigma \Rightarrow \frac{l}{A} = 1$ Ⓓ

④ As $C \to 0$

$\Lambda \longrightarrow \Lambda^{0}$ Ⓑ

Passage - 3

① $\Lambda^{\infty}_{m}(Al_2(SO_4)_3) = 2x + 3y.$

Ⓑ

② $\Lambda^{\infty}_{m(CX)} = \Lambda^{\infty}_{m(BX)} + \Lambda^{\infty}_{m(CA)} - \Lambda^{\infty}_{m(BA)}$

$= 198 + 120 - 140$

$= 178$ ohm^{-1} cm^{2} mole^{-1}

③ $\alpha = \frac{50}{250} = 0.2.$ ⇒ Ⓑ

④ Λ_m increases as c decreases

⇒ Ⓓ

⑤ Ⓓ

Passage - 4

① $E^0_{Y^{2+}|Y} > E^0_{X^{2+}|X}$

& $E^0_{X^{2+}|X} < E^0_{H^+|H_2}$

so $E^0_{X^{2+}|X} < 0$

① Ⓓ

② $E_{cell} = (0.34 + 0.25) - \frac{0.0591}{2} \log \frac{0.1}{1}$

$= 0.6195$ Ⓒ

③ $$E^{\circ}_{Y^+|Y} = \frac{0.34\times 2 - 0.15\times 1}{1}$$

$$= 0.53\ V.$$ Ⓑ

---

① $$\alpha = \frac{10}{200} = \frac{1}{20}$$

$$[H^+] = C\alpha = 0.2\times\frac{1}{20} = 0.01$$

$$pH = 2.$$

② $$\frac{72}{18}\times 2 = \frac{Q}{9\cancel{6500}\ F}$$

$$\Rightarrow Q = 8\ F.$$

③ $$V_{Cl_2} = \frac{5\times 200\times 60}{96500}\times\frac{1}{2}\times 22.4$$

$$\simeq \cdot 7\ L$$

④ $$\frac{115}{23}\cancel{\times}\times 1 = \frac{Q}{F} \Rightarrow Q = 5F$$

[illegible]

Level - 2 Typing done

Electrochemistry ①

1) The overall Reaction is.

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

2 moles of e^- are Involved in the Reaction,

for 2 moles of H_2SO_4.

$\therefore$ Eq wt of H_2SO_4 = mol wt of $H_2SO_4 = 98$

no of Eq of H_2SO_4 present in 3.5 litres of solution

of a Charged. battery

$$= \frac{39}{98} \times \frac{1.294}{100} \times 3500$$

$$= \boxed{18.02}$$

no of Equivalents of H_2SO_4 present in 3.5 litres

of solution after getting discharged

$$= \frac{20}{98} \times \frac{1.139}{100} \times 3500$$

$$= \boxed{8.13}$$

no of eq of H_2SO_4 lost = ~~18.02 — [illegible]~~

$18.02 - 8.13 =$

$= 9.68$

[illegible]

moles of electric charge produced by the battery ②

$$= 9.88\,F$$

$$= 9.88 \times 96500 \text{ Coloumbs}$$

$$= 9.88 \times 96500 \text{ amp seconds}$$

$$= \frac{9.88 \times 96500}{60 \times 60} \text{ amp hours}$$

$$= \boxed{265 \text{ amp hours}}$$

② There is is an increase in mass at the cathode due to deposition of Cu and loss in mass at anode due to loss of Cu and Fe because of oxidation

$$Cu - Cu^{++} + 2e^-$$

$$Fe - Fe^{2+} + 2e^-$$

thus gain in wt at cathode is due to deposition of Cu = [illegible] = 22.011

mole of Cu deposited at cathod $= \frac{22.011}{63.5}$

$= 0.3466$

Equivalent of Cu and Fe dissolved at anode

= it

$$= \frac{140 \times 4825}{96500} = 0.70$$

moles of Fe and Cu dissolved at anode

$$= \frac{0.70}{2} = 0.35$$

moles of Fe dissolved at anode

$$= 0.35 - 0.3466$$
$$= 0.0034$$

~~wt~~ of Fe dissolved at anode $= 0.35 - 0.3466$
moles
$$= 0.0034$$

wt of Fe dissolved $= 0.0034 \times 56 = 0.190\,g$

thus weight loss at anode of 22.260 g contains ~~22.011 g Cu, 0.190~~

22.011 g Cu, 0.190 g Fe and

$(Au + Ag) = 22.260 - 22.011 - 0.190$

$= 0.059\,g$ ~~Fe and~~

$$\% \, Cu = \frac{22.011}{22.26} \times 100 = \boxed{98.88\%}$$

$$\% \, Fe = \frac{0.190}{22.26} \times 100 \quad 0.85\% .$$

③

Rea

Cathode $Cu^{2+} + 2e^- \rightarrow Cu$

anode $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

$pH = 1 \Rightarrow [H^+] = 0.1$

$\Rightarrow n_{H^+} = 0.1 \times 0.1 = 0.01$

$\Rightarrow n_{e^-}$ used $= 0.01$

$\Rightarrow n_{Cu}$ produced $= \frac{0.01}{2} = 0.005$

$\Rightarrow n_{Cu^{2+}}$ left $= 0.1M - 0.005$

$(0.01M - 0.005) \times 1 \frac{35}{1000} \times 0.04 \times 1$

$\Rightarrow$ ~~$M = 0.6M$~~

$\Rightarrow M = 0.64\,M$

$n_{e^-} = 0.01 = \frac{80}{100} \times \frac{0.965 \times t}{96500}$

$t = 1250$ sec

⑤ ANODE REACTION

(i) $2H_2SO_4 \text{ —— } H_2S_2O_8 + 2H^+ + 2e^-$

(ii) $2H_2O \text{ —— } 4H^+ + O_2 + 4e^-$

Cathode Reaction

$2H_2O + \longrightarrow 4H^+ + O_2 + 4e^-$

Equivalents of $H_2S_2O_8$ + Equivalents of O_2 = Equivalents of H_2

$22.4 \text{ L of } H_2 = 1 \text{ mole} = 2 \text{ eq}$

$9.72 \text{ L } H_2 = \frac{2 \times 9.72}{22.4} = 0.868 \text{ eq of } H_2$

$22.4 \text{ L of } O_2 = 1 \text{mole} = 4 \text{ Eq}$

$2.35 \text{ litre of } O_2 = \frac{4 \times 2.35}{22.4} \text{ Eq} = 0.42 \text{ Eq } O_2$

Equivalents of $H_2S_2O_8$ = Eq of H_2 - Eq of O_2

$= 0.868 - 0.420 = 0.448$

$$\frac{W_{H_2S_2O_8}}{194/2} = 0.448$$

$$\boxed{W_{H_2S_2O_8} = 43.4 \text{ g}}$$

⑥ At Cathode

$$O_2 + 2H_2O + 4e^- — 4OH^-$$

At anode

$$H_2 + 2OH^- — 2H_2O + 2e^-$$

mole of H_2 reacting $= \frac{67.2}{22.4} = 3$

Eq of H_2 used up $= 3 \times 2 = 6$

$$\frac{w}{E} = \frac{it}{96500} \quad 6 = \frac{i \times 15 \times 60}{96500}$$

$$\boxed{i = 643.33 \text{ ampere}}$$

Eq of H_2 = Eq of Cu formed

Eq of Cu deposited $= 6$

$$\boxed{W_{Cu} = \frac{6 \times 63.5}{2} = 190.5}$$

⑦ $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$

0.1M

$\frac{0.1 \times 10}{100}$ $\frac{0.1 \times 90}{100}$

Ecell: $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$$E_{RP} = E^0_{RP\,MnO_4^-/Mn^{2+}} - \frac{0.0591}{5} \log \frac{Mn^{2+}}{[MnO_4^-][H^+]^8}$$

$$1.51 - \frac{0.0591}{5} \log \frac{\frac{0.1 \times 90}{100}}{\frac{0.1 \times 10}{100} \times (\cancel{10^8} \times (0.08)^8}$$

$\boxed{1.441}$

$= 1.395$

⑧

$AgI_{(s)} + e^- \longrightarrow Ag + I^-$

$\Rightarrow \quad Ag \longrightarrow Ag^+ + e^- \qquad E = 0.80$

$e^- + AgI \longrightarrow Ag + I^- \qquad E^\circ = ?$

$AgI_{(s)} \longrightarrow Ag^+ + I^-$

~~$0 = 0.80 + E^\circ_{op}$~~ $\cdot\ E_{cell} = 0 \qquad AgI \rightarrow Ag^+ + I^-$

~~$0 = 0.80$~~ .

$$0 = -0.80 + E^\circ_{RP\ I^-/AgI/Ag} + \frac{0.059}{1} \lg \frac{1}{[Ag^+][I^-]}$$

$$E^\circ_{RP\ I^-/AgI/Ag} = \overset{0.7991}{\cancel{0.80}} + \frac{0.059}{1} \lg Ksp_{AgI}$$

$$= \overset{0.7991}{\cancel{0.80}} - 0.059 \times 16.07$$

$= \cancel{0.14\ V}$

$= -0.15\ V$

⑨ $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

$$K_f = 1\times10^{12} = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

$$= \frac{1}{x(2)^4}$$

$$x = 6.25\times10^{-14}\,M$$

~~Note~~ as most all the Cu^{2+} ions are converted to $Cu(NH_3)_4^{2+}$

$$E_{cell} = E^o_{cell} = \underset{Zn/Zn^{2+}}{E^o_{op}} + \underset{Cu^{2+}/Cu}{E^o_{RP}} + \frac{0.0591}{2}\log_{10}\frac{Cu^{2+}}{Zn^{2+}}$$

$$= 0.76 + 0.34 + \frac{0.0591}{2}\log_{10}\frac{6.25\times10^{-14}}{1}$$

$$E_{cell} = \boxed{0.71\,V}$$

⑩

$Ag(NH_3)_2^+ \longrightarrow Ag^+ + 2NH_3 \qquad K = 6\times10^{-8}$

$Ag^+ + e^- \longrightarrow Ag \qquad K = 10^{\frac{0.799}{0.0591}}$

$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3$

$$K = 6\times10^{-8} \times 10^{\frac{0.799}{0.059}}$$

$$E^0 = \frac{0.0591}{1} \cdot \log K$$

$$= 0.373\,V$$

⑪

$$E^{\circ}_{Sn|Sn^{4+}} = \frac{0.136 \times 2 - 0.154 \times 2}{4}$$

$$= -0.009\,V$$

$$E^{\circ}_{cell} = 1.33 - 0.009\,V$$

$$= 1.321\,V$$

$$K = 10^{\frac{12 \times 1.321}{0.0591}} \approx 10^{268}$$

⑫

$$Tl^{+} + 2Co^{3+} \longrightarrow 2Co^{2+} + Tl^{3+}$$

initial 2.5 mmol 5 mmol

eq x $2x$ ~5 mmol 2.5 mmol

$$K = 10^{\frac{2 \times (1.84 - 1.25)}{0.0591}} = \frac{(5)^2 \times 2.5}{x \times (2x)^2}$$

$$10^{20} = \frac{5^2 \times 2.5}{4x^3}$$

$[Tl^{3+}] = 0.05$

$[Co^{2+}] = 0.1$

$$x = 5.386 \times 10^{-7}$$

⑬ for I part of electrolysis

Anode $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

Cathode $Cu^{2+} + 2e^- \longrightarrow Cu$

Eq of O_2 formed = Eq of Cu

$$= \frac{0.4\times 2}{63.6} \approx 12.58\times10^{-3}$$

For II part

Cu^+ ions are discharged completely and thus further passage will lead

Anode $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

Cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$$\text{Eq of } H_2 = \text{Eq of } O_2 = \frac{it}{96500} = \frac{1.2\times7\times60}{96500}$$

$$= 5.22\times10^{-3}$$

∴ Total Eq of O_2

$= 5.22\times10^{-3} + 12.58\times10^{-3}$

$= 17.8\times10^{-3}$

4 Eq of O_2 at NTP = 22.4 L

17.8×10^{-3} Eq of O_2

= 99.68 ml

Eq of $H_2 = 5.22\times10^{-3}$

∴ 2 Eq of H_2 at NTP

= 22.4 L

∴ 5.22×10^{-3} Eq at NTP

$= \boxed{58.46 \text{ ml}}$

(14)

n_{e^-} required $= \frac{100}{34} \times 2$ ~~per~~ hr

~~Curre~~ $= \frac{1000}{34} \times \frac{2}{3600}$ per sec

Current reqd $= \frac{100}{34} \times \frac{2}{3600} \times 96500$ A

so $I = \frac{100}{34} \times \frac{2}{3600} \times 96500 \times 2$

$= 315.36$ A

~~⑯~~

⑮

$$n_e = \frac{5 \times 2 \times 3600}{96500} = 0.373$$

$$wt_{left} = 100 - 0.373 \times 108 \times \frac{100}{95}$$

$$= 57.589\ g.$$

⑯ $$\frac{8.2 \times 10^{12} \times 1000}{18} \times 2 = \frac{1.5 \times 10^{6}}{96500} \times t$$

$$t = 5.86 \times 10^{13}\ \text{sec}$$

$\cong 1.9$ million years.

⑰ Cell Constant $= \dfrac{0.50}{1.50} = \dfrac{1}{3}$

Specific Conductance $= \dfrac{\text{Eq conductance}}{\text{Volume (cc) contain 1 eq}}$

$= \dfrac{97.1}{10000}$ (For 0.1N solution

0.00971 mho cm^{-1}

[Conductance = Specific conductance / cell constant

$= \dfrac{0.00971}{\frac{1}{3}} = 0.02913$ mho

resistance $= \dfrac{1}{0.0249}$ ohm

not type

Current in amp $= \dfrac{PD}{\text{resistance}}$

$= \dfrac{5}{1/0.029} = \boxed{0.1416 \text{ ampere}}$

⑱

$$\frac{73.52}{96500} = \frac{\frac{\text{dist moved}}{2\times3600}}{6/10}$$

$$\text{dist} = 3.29 \text{ cm}$$

⑲ $$1.342 = \frac{1}{170.5} \times \frac{l}{1.86\times10^{-4}}$$

$$l = 4.25 \times10^{-2} \text{ m.}$$

⑳ $$(59.46+79.8) = (1.482\times10^{-4} - 1.5\times10^{-6})\times\frac{100}{S}$$

$$S = 1.0534\times10^{-3} \text{ M}$$

$$= 0.1934 \text{ g/L}$$

㉑ $$0.061 = 0.23 - \frac{0.0591}{2}\log\frac{1}{[SO_4^{2-}]\times2.5\times10}$$

$$\Rightarrow [SO_4^{2-}] = 7.47\times10^{-2} = 0.6\alpha$$

㉒

~~$\Delta S^\circ =$~~

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ $\Delta H = -56700$

$H_2O \rightarrow H^+ + OH^-$ $\Delta H = 19050$

$H_2 + \frac{1}{2} O_2 \rightarrow H^+ + OH^-$ $\Delta H =$

$= -37650$ cal/mo

$\Delta S = 2 \times 96500 \times 0.001158$

$= 223.49$ J/K-mole

$\Delta G = \Delta H - T\Delta S$

$= -223.98$ kJ/mole

$E^\circ = 1.16$ V

④ ~~$n_e = \frac{5\times10\times3600}{96500}$~~

④

$$[S^{2-}] = \frac{10^{-8}\times1.1\times10^{-13}\times0.1}{10^{-6}}$$

$$= 1.1\times10^{-16}$$

$$E^0 = 0.8 + \frac{0.059}{2}\log 2\times10^{-49}$$

$$= -0.6366$$

$$E = -0.6366 - \frac{0.059}{2}\log 1.1\times10^{-16}$$

$$= -0.1658\ \text{V}.$$

(23)

$$E^\circ = 0.28 - 0.699$$

$$= -0.419$$

$$E = -0.419 - \frac{0.0591}{1} \log [H^+]$$

ko

ⓐ $E = -0.419 + 0.0591 \times 5$

$$= -0.124$$

ⓑ $pH = ~~0.0~~ \frac{0.419}{0.059} = 7.1$

ⓒ $pH = 7.5$

$$E = (-0.419 + 0.059 \times 7.5) > 0$$

⇒ spontaneous.

+ve electrode ⇒ calomel.

(26) $n_e = x = n_{H_2SO_4}$ used

$$1 \times 1261 \times \frac{34.5}{100} - 98x = \frac{27}{100} \times (1 \times 1261 - 80x$$

$$435.05 - 98x = 340.47 - 21.6x.$$

$$x = 1.238.$$

(27) $K_{KCl} = \frac{138 \times 0.02}{1000} = 2.76 \times 10^{-3}$

$$\frac{l}{A} = K_{KCl} \times \cancel{A}\ R.R = \cancel{25.3}\,92.$$
$$= 0.2346$$

~~K_{Pw}~~ =

$$K_{Pw} = \frac{0.2346}{9200} = 2.55 \times 10^{-5}$$

$$K_{(Pw + NaCl)} = \frac{0.2346}{7600} = 3.0868 \times 10^{-5}$$

$$K_{NaCl} = 5.3684 \times 10^{-6}$$

$$126.5 = 5.3684 \times 10^{-6} \times 1000$$

$M = 4.2438 \times 10^{-5} = \frac{500}{58.5 V}$

$\therefore V = 2.014 \times 10^{5}\ L$

㉘ $(86 \times 2) + 444 = (2.06 \times 10^{-6} - 4.1 \times 10^{-7}) \times \frac{1000}{S}$

$S = 2.6786 \times 10^{-6}$

$K_{sp} = 7.6872 \times 10^{-17}$

(24) For | cathode

$$2Ce^{4+} + Sn^{2+} \longrightarrow Sn^{4+} + 2Ce^{3+}$$

i 1 mmol 2 mmol

f ~0 1.5 mmole 0.5 mmol 1 mmol.

$$E_{cathode} = E_{Sn^{4+}|Sn^{2+}} = 0.154 - \frac{0.059}{2} \log \frac{1.5}{0.5}$$

$$= 0.1399$$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= 0.1399 - 0.242 = -0.102\ V$$

At eq

$$2Ce^{4+} + Sn^{2+} \longrightarrow Sn^{4+} + 2Ce^{3+}$$

i 4 mmol 2 mmol

f ~~2x~~ $4-2x$ ~~x~~ $2-x$ ~~2 mmol~~ x ~~4 mmol~~ $2x$ $(x \simeq 0)$

$$K = 10^{\frac{2 \times 1.286}{0.059}} = \frac{\cancel{2 \times (4)^2}}{\cancel{4x^3}} \quad \left(\frac{x}{2-x}\right)^3$$

~~$\Rightarrow x \simeq 5.88 \times 10^{-15}$~~ $\frac{x}{2-x} = 3.3968 \times 10^{14}$

$$E_{cathode} = 0.154 - \frac{0.059}{2} \log \left(\frac{2-x}{x}\right)$$

㉕ Before end pt

$$Cr_2O_7^{2-} + 6Cu^{+} + 14H^{+} \longrightarrow 2Cr^{3+} + 6Cu^{2+} + 7H_2O$$

i $\quad 0.05V \quad 6\text{ mmol} \quad ~~10~~$

f $\quad \sim 0 \quad 6-0.3V \qquad 0.1V \quad 0.3V$

$$E_{cathode} = ~~0.340~~\ 0.153 - \frac{0.059}{1}\log\frac{6-0.3V}{0.3V}$$

$$E_{cell} = 0.153 - \frac{0.059}{1}\log\left(\frac{6-0.3V}{0.3V}\right) - 0.242$$

(a) $V = 5\text{ ml}$

$E_{cell} = -0.117$

(b) $V = 10\text{ ml}$

$E_{cell} = -0.089$

(c) $V = 15\text{ ml}$

$E_{cell} = -0.061\text{ V}$

At end pt

$$Cr_2O_7^{2-} + 6Cu^{+} + 14H^{+} \longrightarrow 2Cr^{3+} + 6Cu^{2+} + 7H_2O$$

i $\quad 1\text{ mmol} \quad 6\text{ mmol}$

f $\quad 1-x \quad 6(1-x) \qquad 2x \quad 6x$

$$K = 10^{\frac{6\times 1.177}{0.059}} = \frac{\left(\frac{2x}{45}\right)^2\left(\frac{6x}{45}\right)^6}{}$$

$x \simeq 1$

$$10^{119.69} = \frac{2^2 \times \text{[illegible]}}{(1-x)^7 \times 45}$$

$$(1-x) = \left(\frac{4}{45 \times 10^{119.69}}\right)^{1/7}$$

$$= 5.63 \times 10^{-18}$$

$$E_{cathode} = 0.153 - 0.059\left(\frac{1-x}{1}\right)$$

$$= 1.1707$$

$$E_{cell} = 0.929\ V.$$

Eletro Chemistry Subjective

Q. 1 Write the half-cell reaction for the following cells:

(a) Pt (s) | Ti^{3+}, Ti^{4+} || Fe^{3+}, Fe^{2+} | Pt (s) → Correction??

(b) Pb(s) | $PbSO_4$(s) | SO_4^{2-} || Zn^{2+} | Zn(s)

(c) Pt(s) | Hg(*l*), Hg_2Cl_2 | Cl^- || H^+ | H_2, Pt(s)

(d) Pt(s) | QH_2, Q, H^+ || Cl^- | AgCl(s) | Pt(s) → Ag (s)

QH_2 = Hydroquinone and Q = Quinone

a) A: $Ti^{3+} \rightleftharpoons Ti^{4+} + 1e^-$

C: $Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$

b) A: $SO_4^{2-} + \underset{(s)}{Pb} \rightleftharpoons \underset{(s)}{PbSO_4} + 2e^-$

C: $\underset{(aq.)}{Zn^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Zn}$

c) A: $2\underset{(l)}{Hg} + 2Cl^- \rightleftharpoons Hg_2Cl_2$

C: $\underset{(aq.)}{2H^+} + 2e^- \rightleftharpoons \underset{(g)}{H_2}$

d) A: $(QH_2 \rightleftharpoons 2e^- + Q + 2H^+)$

C: $AgCl + 1e^- \rightleftharpoons Ag + Cl^-$

Q.2 Write the electrochemical notations for the following reactions:

(a) $H_2(g) + Cu^{2+} \rightarrow 2H^+ + Cu(s)$

(b) $Cl_2(g) + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2Cl^-$

(c) $Zn(s) + 2AgCl(s) \rightarrow 2Ag(s) + ZnCl_2$

(d) $[Fe(CN)_6]^{3-} + \frac{1}{2} H_2(g) \rightarrow [Fe(CN)_6]^{4-} + H^+$

a) $Pt, \underset{(g)}{H_2} \mid H^+ \parallel \underset{(aq.)}{Cu^{2+}} \mid \underset{(s)}{Cu}$

b) ~~$\underset{(aq.)}{Fe^{2+}} \mid \underset{(aq.)}{Fe^{3+}} \parallel \underset{(g)}{Cl_2}, Pt \mid \underset{(aq.)}{Cl^-}$~~ $\rightarrow$ $Fe^{2+} \mid Fe^{3+} \parallel Cl^- \mid Cl_2 \mid$

c) ~~$\underset{(s)}{Zn} \mid \underset{(aq.)}{ZnCl_2} \parallel \underset{(s)}{AgCl} \mid \underset{(s)}{Ag}$~~ $Zn \mid Zn^{2+}, Cl^- \mid AgCl \mid Ag$

~~d) $[Fe(CN)_6]^{3-} \mid$ Fe C~~

d) $Pt, \underset{(g)}{H_2} \mid H^+ \parallel [Fe(CN)_6]^{3-}, [Fe(CN)_6]^{4-} \mid Pt.$

Correction in Data

$E^0_{MnO_4^-/Mn^{2+}} = 1.51V$

{ $E_{MnO_4^-/Mn^{2+}}$ ↓ should be given)

Q.3 Q. Answer whether the following reactions will occur spontaneously or not, under standard condition.

(a) will Fe reduces Fe^{3+} to Fe^{2+}? E^o (Fe^{2+}/Fe) = −0.44 V and E^o (Fe^{3+}/Fe^{2+}) = 0.77V

~~(b) will permanganate ion liberate O_2(g) from water in acidic medium? E^0 (O_2, H_2O/H^+) = 1.22 V~~

(c) will O_2 (g) oxidizes gold to $Au(CN)_2^-$ in presence of CN^-(aq) and OH^- (aq)?

E^o [$Au(CN)_2^-$/Au, CN^-] = −0.60 V and E^o (O_2/OH^-, H_2O) = 0.40 V.

(d) would you use silver spoon to stir a solution of $Cu(NO_3)_2$?

E^o (Ag^+ / Ag) = 0.80 V and E^o (Cu^{2+} | Cu) = 0.34 V

(e) reaction of Pb with $AgNO_3$. E^o (Ag^+/Ag) = 0.80 V and E^o (Pb^{2+}/Pb) = −0.126V

(f) will Sn reduce Fe^{3+} to Fe^{2+}? E^o (Fe^{3+}/Fe^{2+}) = 0.77 V and E^o(Sn^{2+}/Sn) = 0.15 V

a) $Fe^{3+} + Fe \rightleftharpoons Fe^{2+}$

A: $Fe \rightleftharpoons Fe^{2+} + 2e^-$ C $Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$

$$E^0_{cell} = E^0_{Fe^{3+}/Fe^{2+}} - E^0_{Fe^{2+}/Fe}$$

$$= 0.77 - (-0.44) = +1.21 V$$

∴ $\boxed{\text{spontaneous}}$

Ans. $\boxed{\text{Will Reduce}}$

~~b)~~

~~$MnO_4^- + H_2O \rightarrow Mn^{2+} + O_2$~~

~~$E^0_{cell} = E^0_{MnO_4^-/Mn^{2+}} - E^0_{O_2/H_2O}$~~

~~$= 1.51 - 1.22 = 0.29$~~

~~$\boxed{\text{Spontaneous}}$~~

b)

$Au + O_2 \rightarrow OH^- + [Au(CN)_2]^-$

$E^0_{cell} = E^0_{O_2} - E^0_{Au(CN)_2^-/Au}$

c) $2Ag + Cu^{2+} \rightleftharpoons Cu + 2Ag^{+}$

$E^{\circ}_{cell} = E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Ag^{+}/Ag}$

$0.34 - 0.8 = -ve$ (not spontaneous)

∴ $\boxed{\text{can be used}}$

d) $Pb + Ag^{+} \rightleftharpoons Ag + Pb^{2+}$

$E^{\circ} = E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Pb^{2+}/Pb}$

$= 0.8 - (-0.126) = .926V = +ve$ (spontaneous)

e) $Fe^{3+} + Sn \rightarrow Fe^{2+} + Sn^{2+}$

$= E^{\circ}_{Fe^{3+}/Fe^{2+}} - E^{\circ}_{Sn^{2+}/Sn}$

$= 0.77 - 0.15 = 0.62\ V$

$= +ve$ (Spontaneous)

✓ ✓

Q. 4 For the cell reaction $2Ce^{4+} + Co \rightarrow 2Ce^{3+} + Co^{2+}$

E°_{cell} is 1.89 V. If $E^\circ_{Co^{2+}|Co}$ is – 0.28 V, what is the value of $E^\circ_{Ce^{4+}|Ce^{3+}}$?

C: $\left(Ce^{4+} + 1e^- \rightleftharpoons Ce^{3+}\right) \times 2$

A: $\underset{(s)}{Co} \rightleftharpoons Co^{2+} + 2e^-$

cell eqⁿ: $2Ce^{4+} + \underset{(s)}{Co} \rightleftharpoons Co^{2+} + 2Ce^{3+}$

$$E^0_{cell} = SRP_C - SRP_A$$

$$1.89 = E^0_{Ce^{4+}/Ce^{3+}} - E^0_{Co^{2+}/Co}$$

$$1.89 + E^0_{Co^{2+}/Co} = E^0_{Ce^{4+}/Ce^{3+}}$$

$$\boxed{E^0_{Ce^{4+}/Ce^{3+}} = 1.61\ V}$$

Q.5 Determine the standard reduction potential for the half reaction :

$Cl_2 + 2e^-$ ⍰→ $2Cl^-$

Given $Pt^{2+} + 2Cl^- \rightarrow Pt + Cl_2$, $E° = -0.15\ V$

$Pt^{2+} + 2e^- \rightarrow Pt$ $E° = 1.20\ V$

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^0_{Cl_2/Cl^-}$$

$$Pt^{2+} + Cl^- \rightarrow Pt + Cl_2$$

$$E^0_{cell} = E^0_{Pt^{2+}/Pt} - E^0_{Cl_2/Cl^-}$$

$$-0.15 = 1.20 - E^0_{Cl_2/Cl^-}$$

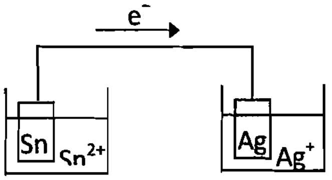
$$\boxed{E^0_{Cl_2/Cl^-} = 1.35\ V}$$

✓

Qb a. Write cell reaction for the following cell and determine standard state emf of the cell

E^o (Ag^+/Ag) = 0.80 V

E^o (Sn^{2+}/Sn) = −0.14 V



A:· $Sn_{(s)} \rightleftharpoons Sn^{2+} + 2e^-$

C: $(Ag^+ + 1e^- \rightleftharpoons Ag_{(s)}) \times 2$

B. Cell eq^n

$2Ag^+ + Sn_{(s)} \rightleftharpoons Sn^{2+} + 2Ag_{(s)}$

$$\boxed{E^o_{cell} = (0.8 + 0.14) = 0.94\,V}$$

Q.7 Given the standard reduction potentials Tl⁺ + e⁻ → Tl, E° = -0.34 V and Tl³⁺ + 2e⁻ → Tl⁺, E° = 1.25V. Examine the sponaneity of the reaction, 3Tl⁺ → 2Tl + Tl³⁺. Also find E° for this disproportionation.

$Tl^{+} + 1e^{-} \rightleftharpoons Tl \qquad E^{0} = -0.34$

$E^{0}_{Tl^{+}/Tl} = -0.34\ V$

$Tl^{3+} + 2e^{-} \rightleftharpoons Tl^{+}$

$E^{0}_{Tl^{3+}/Tl^{+}} = 1.25\ V$

$3Tl^{+} \rightleftharpoons 2Tl + Tl^{3+}$

C: $Tl^{+} + 1e^{-} \rightleftharpoons Tl$ | A: $Tl^{+} \rightleftharpoons Tl^{3+} + 2e^{-}$

$E^{0} = SRP_{C} - SRP_{A}$

$= E^{0}_{Tl^{+}/Tl} - E^{0}_{Tl^{3+}/Tl^{+}}$

$= -0.34 - (1.25)$

$= \boxed{-1.59\ V}$

non spontaneous

Q.⑧ Calculate the equilibrium constnant for the reactin Fe + CuSO$_4$ ⇔ FeSO$_4$ + Cu at 25°C. Given E° (Fe/Fe^{2+}) = 0.44 V, E°(Cu/Cu^{2+}) = -0.336 V.

$\underline{\underline{C}}$: $Cu^{2+} + 2e^- \rightleftharpoons Cu$ | $\underline{\underline{A}}$ $Fe \rightleftharpoons Fe^{2+} + 2e^-$

$$E^\circ_{cell} = SRP_C - SRP_A$$
$$= 0.336 - (-0.44)$$
$$= 0.776$$

~~At eq^m, $E^\circ_{cell} = -\frac{0.059}{2} \log K$~~

~~$\log K = -3.52$~~

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log Q$$

At eq^m, $E_{cell} = 0$, $Q = K$

$$0.776 \leftarrow E^\circ_{cell} = \frac{0.059}{2} \log K$$

$$\boxed{K = 2.01 \times 10^{26}}$$

Q. 9 For a cell Mg(s) | Mg^{2+}(aq) || Ag^{+}(aq) | Ag. Find the maximum work that can be obtained by operating the cell. E°(Mg^{2+}/Mg) = -2.37V, E°(Ag^{+}/Ag) = 0.8 V.

$$\underline{\underline{A}}: \quad Mg_{(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2e^-$$

$$\underline{\underline{C}}: \quad (Ag^{+}_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)}) \times 2$$

$$2Ag^{+}_{(aq)} + Mg_{(s)} \rightleftharpoons Mg^{2+} + 2Ag_{(s)}$$

$$E^{0}_{cell} = E^{0}_{Ag^{+}/Ag} - E^{0}_{Mg^{2+}/Mg}$$

$$E^{0}_{cell} = 0.8 - (-2.37) = 3.17V$$

$$\text{Max. Work} = -nFE^{0}_{cell}$$

$$= \boxed{-611{,}810 \text{ J.}}$$

Q.10 The standard reduction potential at 25°C for the reduction of water

$2H_2O + 2e^- \Leftrightarrow H_2 + 2OH^-$ is -0.8277 volt. Calculate ΔG° & the equilibrium constant for the reaction

$2H_2O \Leftrightarrow H_3O^+ + OH^-$ at 25°C.

① $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $\quad E_1^\circ = -0.8277$

$n_1 = 2$

Now, we have to add a half r^n ~~that~~ to eq^n ①, such that when added to eq^n ①, we get full cell r^n

$2H_2O \rightleftharpoons H_3O^+ + OH^-$ ③

~~or ③ $2H_2O \rightleftharpoons H^+ + OH^-$~~

~~$2H^+ + 2e^- \rightleftharpoons H_2$~~

Add Half r^n:

$H_2 \rightleftharpoons 2H^+ + 2e^-$ $\quad E_2^\circ$

or

② $H_2 + H_2O \rightleftharpoons 2H_3O^+ + 2e^-$ $\quad E_2^\circ = 0$

① + ② = ③

$$\Delta G_1^\circ + \cancel{\Delta G_2^\circ} = \Delta G_3^\circ$$

$$-n_1 F E_1^\circ = \Delta G_3^\circ$$

$$\Delta G_3^\circ = -2 \times (96500)(-0.8277)$$

Also

$$\Delta G^\circ = -2.303RT \log K$$

$$\frac{159746.1}{2} = -2.303 \times (8.314)(298) \log K$$

~~log K = [illegible]~~

$$K = 10^{-7}$$

∴ K for the eqⁿ

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \boxed{K_w^2 = 10^{-14}}$$

Q.11 At 25°C the value of K for the equilibrium $Fe^{3+} + Ag \Leftrightarrow Fe^{2+} + Ag^{+}$ is 0.531 mol/litre. The standard electrode potential for $Ag^{+} + e \Leftrightarrow Ag$ is 0.799V. What is the standard potential for $Fe^{3+} + e \Leftrightarrow Fe^{2+}$?

$$E^{\circ} = +\frac{0.059}{1} \log K.$$

$$E^{\circ} = -0.016$$

$$Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^{+}$$

$$-0.016 = E^{\circ}_{Fe^{3+}/Fe^{2+}} - \underbrace{E^{\circ}_{Ag^{+}/Ag}}_{0.799}$$

$$\boxed{E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.783\,V}$$

Oxid^n ~~or red^n → must~~ be specified.

$E^\circ_{Zn^{2+}/Zn} = -0.76$ Check !!

$E^\circ_{Cu^{2+}/Cu} = 0.34$

Q. 12 The normal potential of Zn referred to SHE is 0.76V and that of Cu is -0.34V at 25°C. When excess of Zn is added to $CuSO_4$, Zn displaces Cu^{2+} till equilibrium is reached. What is the ratio of Zn^{2+} to Cu^{2+} ions at equilibrium?

C : $Cu^{2+} + 2e^- \rightleftharpoons Cu$

A : $Zn \rightleftharpoons Zn^{2+} + 2e^-$

cell eq^n $\underset{(s)}{Zn} + Cu^{2+} \rightleftharpoons Zn^{2+} + \underset{(s)}{Cu}$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$$

$$= +0.34 - (-0.76) = 1.1$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log Q$$

At eq^m, $E_{cell} = 0$, $Q = K$

$\therefore$ ~~$E^\circ_{cell} = \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$~~

$$\therefore \underset{\underset{1.1}{\parallel}}{E^\circ_{cell}} = \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$[Zn^{2+}]$ $\times 10^{37}$

Correction
in Q in
part C

Check Ans for ⓒ

(Q.13) ~~Q~~ Consider the following sequence of reactions occurring in the acid medium. All emf (standard) are measured at 25°C and expressed in volt unit:

$$MnO_4^- \xrightarrow{0.564} MnO_4^{2-} \xrightarrow{2.26} MnO_2 \xrightarrow{0.95} Mn^{3+} \xrightarrow{1.51} Mn^{2+} \xrightarrow{-1.18} Mn$$

(a) Determine E^o for : $MnO_4^- \rightarrow Mn^{2+}$

(b) Which will be the better oxidizing agent in acid medium—MnO_4^- or MnO_4^{2-} when the final form of manganese is Mn^{2+}?

(c) ~~Determine the standard emf of the following reaction:~~ Correction MnO_4^-

$$3MnO_4^{2-} + 4H^+ \rightarrow MnO_2(s) + 2MnO_4^{\boxed{2-}} + 2H_2O$$

① $MnO_4^- + 1e^- \rightarrow MnO_4^{2-}$ $\quad E_1^0 = 0.564, n_1 = 1$

② $MnO_4^{2-} + 2e^- \rightarrow MnO_2$ $\quad E_2^0 = 2.26, n_2 = 2$

③ $MnO_2 + 1e^- \rightarrow Mn^{3+}$ $\quad E_3^0 = 0.95, n_3 = 1$

④ $Mn^{3+} + 1e^- \rightarrow Mn^{2+}$ $\quad E_4^0 = 1.51, n_4 = 1$

⑤ $Mn^{2+} + 2e^- \rightarrow Mn$ $\quad E_5^0 = -1.18, n_5 = 2$

a) ⑥ $MnO_4^- + 5e^- \rightarrow Mn^{2+}$ $\quad E_6^0 = ?, n_6 = 5$

⑥ = ① + ② + ③ + ④

$$\therefore \Delta G_6^0 = \Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0 + \Delta G_4^0$$

$$+n_6 \cancel{F} E_6^0 = +n_1 \cancel{F} E_1^0 + n_2 \cancel{F} E_2^0 + n_3 \cancel{F} E_3^0 + n_4 \cancel{F} E_4^0$$

$$E_6^0 = \frac{1(0.564) + 2(2.26) + 1(0.95) + 1(1.51)}{5}$$

⑦ $MnO_4^{2-} + 4e^- \rightarrow Mn^{2+}$, $E^\circ_7 = ?$ $n = 4$

$$\therefore 4E^\circ_7 = 2(2.26) + 1(0.95) + 1(1.51)$$

$$E^\circ_7 = \frac{2(2.26) + (0.95) + (1.51)}{4}$$

$$\boxed{E^\circ_7 = 1.745\,V}$$

$\therefore$ $\underline{MnO_4^{2-}}$ is a better O.A.

~~(c) $3MnO_4^{2-} + 4H^+ \rightarrow MnO_{2(s)} + 2MnO_4^- + 2H_2O$~~

~~$\therefore E^\circ_{cell} = SRP_{cathode} - SRP_{Anode}$~~

~~Cathode:~~

~~$MnO_4^{2-} + 2e^- \rightarrow MnO_2$ $E^\circ = 2.26\,V$~~

~~Anode:~~

~~$MnO_4^{2-} \rightarrow MnO_4^- + 1e^-$ $E^\circ = -0.564\,V$~~

~~$\therefore E^\circ_{cell} = 2.26 - 0.564$~~

~~$\boxed{E^\circ_{cell} = 1.696\,V}$~~

✓

Q.14 Calculate the EMF of following cells at 25°C.

(i)	Fe | $FeSO_4$(a = 0.1) || $CuSO_4$ (a = 0.01) | Cu	E°(Fe^{2+}/Fe) = -0.44 V
(ii)	Fe | Fe^{2+} (a = 0.3) || Sn^{2+} (a = 0.1) | Sn	E°(Cu^{2+}/Cu) = +0.34 V
(iii)	Pt, H_2(2atm) | HCl | H_2(10 atm), Pt.	E°(Sn^{2+}/Sn) = -0.14 V

i) A: $\underset{(s)}{Fe} \rightleftharpoons \underset{(0.1)}{Fe^{2+}} + 2e^-$

C: $\underset{0.01}{Cu^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Cu}$

cell: $\underset{(s)}{Fe} + \underset{(0.01)}{Cu^{2+}} \rightleftharpoons \underset{(0.1)}{Fe^{2+}} + \underset{(s)}{Cu}$

$Q = \left(\frac{0.1}{0.01}\right)$, $n=2$, $E^\circ_{cell} = 0.34 + 0.44$

$E_{cell} = 0.78 - \frac{0.059}{2} \log\left(\frac{0.1}{0.01}\right) = 0.78 - 0.0295$

~~Ecell = [illegible]~~ $\boxed{E_{cell} = 0.7505\ V}$

ii) A: $\underset{(s)}{Fe} \rightleftharpoons \underset{(0.3)}{Fe^{2+}} + 2e^-$

C: $\underset{(0.1)}{Sn^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Sn}$

Cell eqn: $\underset{(s)}{Fe} + \underset{(0.1)}{Sn^{2+}} \rightleftharpoons \underset{(s)}{Sn} + \underset{(0.3)}{Fe^{2+}}$

$Q = \left(0.3\right)$, $n=2$, $E^\circ_{cell} =$

$$E_{cell} = 0.30 - \frac{0.059}{2} \log(3) = 0.30 - 0.014$$

$$\boxed{E_{cell} = 0.286\ V}$$

(iii) A: $\underset{(2)}{H_2} \rightleftharpoons \underset{(C)}{2H^+} + 2e^-$

C: $\underset{(C)}{2H^+} + 2e^- \rightleftharpoons \underset{(10)}{H_2}$

Cell eqⁿ: $\underset{(C)}{2H^+} + \underset{(2)}{H_2} \rightleftharpoons \underset{(10)}{H_2} + \underset{(C)}{2H^+}$

$$Q = \left(\frac{10}{2}\right) = (5), \quad n = 2, \quad E^\circ = 0$$

$$E = -\frac{0.059}{2} \log(5)$$

$$\boxed{E = -0.020\ V}$$

Q. 15 What is the electrode potential of Mg^{2+} | Mg electrode at 25°C, in which the concentration of Mg^{2+} is 0.01 M. $E°(Mg^{2+} | Mg) = -2.36$ V.

$$\underset{(0.01)}{Mg^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Mg}$$

Nernst Eq^n:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2} \log \frac{1}{[Mg^{2+}]}$$

$$" = -2.36 - \frac{0.059}{\cancel{2}} \log (10^{2})$$

~~$\boxed{E_{cell} = -0.049\,V}$~~

$$\boxed{E_{cell} = -2.419\,V}$$

Q. 16 Calculate E° and E for the cell Sn | Sn^{2+} (1M) || Pb^{2+} (10^{-3}M)| Pb,

E°(Sn^{2+} | Sn) = -0.14 V, E°(Pb^{2+} | Pb) = -0.13 V. What do you infer from cell EMF?

A: $\underset{}{Sn} \rightleftharpoons \underset{(1M)}{Sn^{2+}} + 2e^-$

C: $\underset{(10^{-3}M)}{Pb^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Pb}$

Cell: $\underset{(10^{-3}M)}{Pb^{2+}} + \underset{(s)}{Sn} \rightleftharpoons \underset{(1M)}{Sn^{2+}} + \underset{(s)}{Pb}$

$E^0_{cell} = SRP_C - SRP_A$

$= -0.13 + 0.14 = \boxed{0.01 = E^0_{cell}}$

$n = 2$, $Q = \frac{1}{10^{-3}} = 10^3$

$E = 0.01 - \frac{0.059}{2} \log(10^3)$

$= 0.01 - 0.0885$

$\boxed{E = -0.0785 V}$

∴ Cell r^n is not spontaneous

To make it spontaneous, the following cell should

Q.17 At what concentration of Cu^{2+} in a solution of $CuSO_4$ will the electrode potential be zero at 25°C? Can the oxidation potential become positive? E° (Cu | Cu^{2+}) = -0.34V.

$$\underset{(aq.)}{Cu^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Cu} \qquad \frac{1}{[Cu^{2+}]} = Q$$

$$E^{\circ} = 0.34\,V \quad , \; n = 2$$

$$0 = 0.34 - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$-11.52 = \log [Cu^{2+}]$$

$$[Cu^{2+}] = 3.01 \times 10^{-12}$$

[Yes, can be +ve depending upon the concn]

~~Calculation~~

Q. ⑱ A zinc electrode is placed in a 0.1 M solution at 25°C. Assuming that the salt is 20% dissociated at this dilution calculate the electrode potential. E°(Zn^{2+} | Zn) = -0.76 V.

$$[Zn^{2+}] = 0.2 \times 0.1$$

$$\underset{\substack{\downarrow \\ 0.2\times 0.1}}{Zn^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Zn}$$

Nernst eqn

$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]}$$

$$E = -0.76 - \frac{0.059}{2} \log\left(\frac{1}{0.02}\right)$$

$$\boxed{E = -0.81V}$$

Q. 19 Calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively. The standard potential of the cell is 1.1 V.

C: $Cu^{2+} + 2e^- \rightleftharpoons Cu$

A: $Zn \rightleftharpoons Zn^{2+} + 2e^-$

$$\underset{(aq.)}{Cu^{2+}} + \underset{(s)}{Zn} \rightleftharpoons \underset{(aq.)}{Zn^{2+}} + \underset{(s)}{Cu}$$

$$E_{cell} = \underbrace{(1.1)}_{E^{\circ}_{cell}} - \frac{0.059}{2} \log \frac{\overset{0.001}{[Zn^{2+}]}}{\underset{0.1}{[Cu^{2+}]}}$$

~~$E_{cell} = 1.185$ V~~

$$\boxed{E_{cell} = 1.159 \text{ V}}$$

Q. 20 Calculate the pH of following solutions.

(i) Pt, H_2| HCl, E = 0.25 V   (ii) Pt, H_2 | H_2SO_4, E = 0.30 V

i) $H_2 \rightleftharpoons 2H^+ + 2e^-$ $E^\circ = 0$

Nernst eqⁿ:

$$0.25 = 0 - \frac{0.059}{\cancel{2}} \log [H^+]^{\cancel{2}}$$

$$\boxed{-\log [H^+] = pH = 4.23}$$

(ii) $H_2 \rightleftharpoons 2H^+ + 2e^-$ $E^\circ = 0$

Neenst Eqⁿ:

$$0.30 = 0 - \frac{0.059}{\cancel{2}} \log [H^+]^{\cancel{2}}$$

$$-\log [H^+] = \boxed{5.08 = pH}$$

Q. 21 The EMF of the cell M | M^{n+}(0.02 M) || H^+(1M) | H_2(g) (1 atm), Pt at 25°C is 0.81V. Calculate the valency of the metal if the standard oxidation of the metal is 0.76V.

$$\underline{\underline{A}}: \quad (M \rightleftharpoons M^{n+} + ne^-) \times 2$$

$$\underline{\underline{C}}: \quad \left[\underset{(1M)}{2H^+} + 2e^- \rightleftharpoons \underset{(1atm)}{H_2}\right] n$$

$$2nH^+ + 2M_{(s)} \rightleftharpoons 2M^{n+} + nH_2$$

$$0.81 = (0 - (-0.76)) - \frac{0.059}{2 \times n} \log \frac{[M^{n+}]^2}{\underset{\hookrightarrow 1}{[H^+]}^{2n}}$$

$$0.05 = -\frac{0.059}{\cancel{2} \times n} \log \frac{[M^{n+}]^{\cancel{2}}}{[\ ]}$$

$$\boxed{n = 2}$$

Q.22 EMF of the cell Zn | $ZnSO_4$(a = 0.2) || $ZnSO_4(a_2)$ | Zn is -0.0088 V at 25°C. Calculate the value of a_2.

A: $\underset{(s)}{Zn} \rightleftharpoons \underset{(a=0.2)}{Zn^{2+}} + 2e^-$

C: $\underset{(a_2)}{Zn^{2+}} + 2e^- \rightleftharpoons \underset{(s)}{Zn}$

Cell eqn: $\underset{(a_2)}{Zn^{2+}} + \underset{(s)}{Zn} \rightleftharpoons \underset{(a=0.2)}{Zn^{2+}} + \underset{(s)}{Zn}$

$$\therefore \quad Q = \left(\frac{0.2}{a_2}\right)$$

$\therefore$ $E^0_{cell} = 0$, $n = 2$,

Nernst eqn:

$$\underset{\underset{-0.0088}{||}}{E_{cell}} = \cancel{E^0_{cell}} - \frac{0.0591}{2}\log\left(\frac{0.2}{a_2}\right)$$

$$0.298 = \log\left(\frac{0.2}{a_2}\right)$$

$$\boxed{a_2 = 0.1007}$$

Q.23 Equinormal solutions of two weak acids, HA(pKa = 3) and HB(pKa = 5) are each placed in contact with standard hydrogen electrode at 25°C. When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.

HA

(Cathode)

$HA \rightleftharpoons H^+ + A^-$

$\downarrow$

$C_1 = \sqrt{Ka_1 \times C}$

C:

$2H^+ + 2e^- \rightleftharpoons H_2$

(C_1)

HB

(Anode:)

$HB \rightleftharpoons H^+ + B^-$

$\downarrow$

$C_2 = \sqrt{Ka_2 \times C}$

A:

$H_2 \rightleftharpoons 2H^+ + 2e^-$

(C_2)

Cell: $\underset{(C_1)}{2H^+} + H_2 \rightleftharpoons \underset{(C_2)}{2H^+} + H_2$

$E^0_{cell} = 0$, $n = 2$

$$E_{cell} = 0 - \frac{0.059}{\cancel{2}} \log\left(\frac{C_2}{C_1}\right)^{\cancel{2}}$$

$$E_{cell} = -0.059 \log\left(\frac{Ka_1 \times \cancel{C}}{Ka_2 \times \cancel{C}}\right)^{1/2}$$

$Ka_1 = 10^{-3}$, $Ka_2 = 10^{-5}$

$$E_{cell} = -0.059 \log\left(\frac{10^{-3}}{10^{-5}}\right)^{1/2}$$

ⓠ24 In two vessels each containing 500ml water, 0.5 m mol of aniline ($K_b = 10^{-9}$) and 25mmol of HCl a are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

Let this be Cathode

$$\boxed{\frac{\text{Aniline} \; 0.5\times10^{-3}}{0.5}} = C = 10^{-3}$$

$$\underline{\underline{C}}: \; 2H^+ + 2e^- \rightleftharpoons H_2$$

C_1

$$\frac{K_w}{\sqrt{K_b\times C}} = \frac{K_w}{\sqrt{10^{-9}\times10^{-3}}} = \frac{K_w}{10^{-6}}$$

Let this be Anode

$$\boxed{HCl} \rightarrow \frac{25\times10^{-3}}{0.5} = 50\times10^{-3}$$

$$\underline{\underline{A}}: \; H_2 \rightleftharpoons 2H^+ + 2e^-$$

$c_2 = 50\times10^{-3}$

$$\underline{\text{Cell eq}^n}: \; \underset{(C_1)}{2H^+} + H_2 \rightleftharpoons \underset{(C_2)}{2H^+} + H_2$$

$$Q = \left(\frac{C_2}{C_1}\right)^2 = \left(\frac{50\times10^{-3}}{10^{-8}}\right)^2$$

$E^\circ_{cell} = 0$, $n = 2$

$$E_{cell} = 0 - \frac{0.059}{\cancel{2}} \log\left(\frac{50\times10^{-3}}{10^{-8}}\right)^{\cancel{2}}$$

$$= -0.059 \log(5\times10^4) = -0.395V$$

∴ In order to get Ecell value to +ve, the 1st vessel of Aniline should be taken as Anode & the other one as Cathode.

$$\boxed{E^{\circ}_{cell} = 0.395\ V}$$

Q.25 The emf of the cell Ag | AgI | KI(0.05M) || $AgNO_3$(0.022 M) | Ag is 0.769 V. Calculate the solubility product of AgI.

A : $Ag_{(s)} \rightleftharpoons Ag^{+} + 1e^{-}$

$$c_1 = \frac{K_{sp}\,AgI}{(0.05)}$$

C : $Ag^{+} + 1e^{-} \rightleftharpoons Ag_{(s)}$

$$c_2 = 0.022$$

cell : $Ag^{+}_{(c_2)} + Ag_{(s)} \rightleftharpoons Ag_{(s)} + Ag^{+}_{(c_1)}$

$$\therefore \quad Q = \frac{(K_{sp}\,AgI)}{(0.05)\times(0.022)}$$

$$E^{\circ}_{cell} = 0, \quad n = 1, \quad Q = \frac{K_{sp}\,AgI}{(0.05 \times 0.022)}$$

~~Ecell~~ [illegible]

$$E_{cell} = 0.769 = 0 - \frac{0.059}{1}\log\left(\frac{K_{sp}\,AgI}{0.05 \times 0.0}\right.$$

$$\boxed{K_{sp}\,AgI = 1.01 \times 10^{-16}}$$

(Q.26) Consider the cell Ag | AgBr(s) | Br⁻ || AgCl(s) | Cl⁻ | Ag at 25°C. The solubility product constants of AgBr and AgCl are respectively 5×10^{-13} and 1×10^{-10}. For what ratio of the concentrations of Br⁻ and Cl⁻ ions would the emf of the cell be zero?

A:

$$\underset{(s)}{Ag} \rightleftharpoons Ag^+ + 1e^-$$

$$c_1 = \frac{K_{sp}\,AgBr}{[Br^-]}$$

C:

$$Ag^+ + 1e^- \rightleftharpoons \underset{(s)}{Ag}$$

$$c_2 = \frac{K_{sp}\,AgCl}{[Cl^-]}$$

Cell:

$$\underset{(s)}{Ag} + \underset{(c_2)}{Ag^+} \rightleftharpoons \underset{(c_1)}{Ag^+} + \underset{(s)}{Ag}$$

$$\underset{\substack{\| \\ 0}}{E} = \underset{\substack{\| \\ 0}}{E^\circ} - \frac{0.059}{1} \log\left(\frac{c_1}{c_2}\right)$$

$$\therefore \quad c_1 = c_2$$

$$\therefore \quad \frac{K_{sp}\,AgBr}{[Br^-]} = \frac{K_{sp}\,AgCl}{[Cl^-]}$$

$$\frac{[Br^-]}{[Cl^-]} = \frac{K_{sp}\,AgBr}{K_{sp}\,AgCl} = \frac{5 \times 10^{-13}}{1 \times 10^{-10}}$$

Q.27 Calculate the emf of the cell

Pt, H_2(1.0 atm) | CH_3COOH(0.1M) || NH_3(aq. 0.01M) | H_2(1.0 atm), Pt

Ka(CH_3COOH) = 1.8×10^{-5}, K_b (NH_3) = 1.8×10^{-5}.

Anode:

$$\underset{(1atm)}{H_2} \rightleftharpoons \underset{(C_1)}{2H^+} + 2e^-$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$C_1 = \sqrt{K_a \times (0.1)}$$

$$\sqrt{1.8 \times 10^{-5} \times 0.1}$$

Cathode:

$$\underset{(C_2)}{2H^+} + 2e^- \rightleftharpoons \underset{(1atm)}{H_2}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$\sqrt{K_b \times 0.1}$$

$$\therefore [H^+] = C_2 = \frac{K_w}{\sqrt{K_b \times 0.1}} = \frac{K_w}{\sqrt{1.8 \times 10^{-5} \times 0}}$$

Cell eqn:

$$\underset{(1atm)}{H_2} + \underset{(C_2)}{2H^+} \rightleftharpoons \underset{(C_1)}{2H^+} + \underset{(1atm)}{H_2}$$

$$Q = \left(\frac{C_1}{\ }\right)^2$$

Neenst eq^n

$$\therefore E_{cell} = \cancel{E^{\circ}_{cell}} - \frac{0.059}{\cancel{2}} \log\left(\frac{C_1}{C_2}\right)^{\cancel{2}}$$

$$E_{cell} = -0.059 \log\left[\frac{(1.8\times10^{-5}\times0.1)}{K_w}\right]$$

$$E_{cell} = -0.059 \log\left[\frac{18\times10^{-7}}{10^{-14}}\right]$$

$$= -0.059\left[\log 18 + 7\right]$$

$$= -0.059\left[2\log 3 + \log 2 + 7\right]$$

$$= \boxed{-0.46\ V}$$

$$E_{cell} = 0 - \frac{0.059}{1} \log \frac{\frac{\sqrt{1.8\times10^{-5}\times0.1}}{10^{-14}}}{\sqrt{1.8\times10^{-5}\times0.01}}$$

$$= -0.46 V$$

Q.28 The cell Pt, H_2(1atm) | H^+(pH = x) || Normal calomel Electrode has an EMF of 0.67V at 25°C. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is -0.28V.

A: $H_2 \rightleftharpoons 2H^+ + 2e^-$

C: $\underset{(1M)}{Hg_2^{2+}} + 2e^- \rightarrow 2Hg_{(s)}$ (∵ Normal Calomel electrode)

Cell eqn: $Hg_2^{2+} + \underset{(1atm)}{H_2} \rightleftharpoons 2H^+ + 2Hg_{(s)}$

$$Q = [H^+]^2$$

$$E^0_{cell} = \underset{\underset{0.28}{\parallel}}{SRP_C} - \cancel{SRP_A} \leftarrow 0$$

Nernst Eqn

$$\therefore\ 0.67 = 0.28 - \frac{0.059}{\cancel{2}} \log [H^+]^{\cancel{2}}$$

$$\boxed{-\log [H^+] = pH = 6.61}$$

Calculation: (Ans Correction)

Q. 29) Voltage of the cell Pt, H_2(1 atm) | HOCN (10^{-3}M) || Ag^+ (0.8M) | Ag(s) is 1.0006 V. Calculate the K_a for HOCN. Neglect $[H^+]$ because of oxidation of $H_2(g)$.

$Ag^+ + e \rightarrow Ag(s) = 0.8$ V.

A: $\underset{(1\,atm)}{H_2} \rightleftharpoons \underset{C_1}{2H^+} + 2e^-$ $E^0 = 0$

$HOCN \rightleftharpoons H^+ + OCN^-$

[illegible]

$\therefore K_a = 6.7 \times 10^{-5}$

C: $\left(\underset{(0.8M)}{Ag^+} + 1e^- \longrightarrow \underset{(s)}{Ag}\right) \times 2$ $E^0 = 0.8$ V

Cell eqn: $\underset{(0.8)}{2Ag^+} + H_2 \rightleftharpoons \underset{(C_1)}{2H^+} + \underset{(s)}{2Ag}$

$Q = \left(\frac{C_1}{0.8}\right)^2$, $n = 2$

$E^0_{cell} = SRP_C - \cancel{SRP_A} = 0.8$

Nernst Eqn

$$\underset{\overset{\parallel}{E}}{1.006} = \underset{\overset{\parallel}{E^0}}{0.8} - \frac{0.059}{\cancel{2}} \log\left(\frac{C_1}{0.8}\right)^{\cancel{2}}$$

$-3.43 = \log\left(\frac{0.8}{\ }\right)$

2.58×10^{-4}

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{(3{\cdot}185 \times 10^{-4})^2}{10^{-3} - 3{\cdot}185 \times 10^{-4}}$$

$$= 1{\cdot}488 \times 10^{-4}$$

(Correction in values)

{ $E^{\circ}_{Cu^{2+}/Cu}$ should be given }

Q. 30 Calculate the voltage, E, of the cell at 25°C

$Mn(s) \mid Mn(OH)_2(s) \mid$ ~~Mn^{2+} (xM)~~, $OH^-(1.00 \times 10^{-4}\ M) \parallel Cu^{2+}(0.19\ M) \mid Cu(s)$

given that $K_{sp} = 1.9 \times 10^{-13}$ for $Mn(OH)_2(s)$ $E^{\circ}(Mn^{2+}/Mn) = -1.18\ V$

$E^{\circ}(Cu^{2+}/Cu) = 0.34$

A: $Mn_{(s)} \rightleftharpoons \underset{\downarrow}{Mn^{2+}} + 2e^-$

$$c_1 = \frac{K_{sp}\, Mn(OH)_2}{[OH^-]^2}$$

C: $\underset{\downarrow}{Cu^{2+}} + 2e^- \rightleftharpoons Cu_{(s)}$

$c_2 = 0.19$

Cell r^n

$$Mn_{(s)} + \underset{\substack{\downarrow \\ c_2}}{Cu^{2+}} \rightleftharpoons Cu_{(s)} + \underset{\substack{\downarrow \\ c_1}}{Mn^{2+}}$$

$Q = \frac{c_1}{c_2}$, $E^{\circ} = 0.34 + 1.18 = 1.52V$

$$E = 1.52 - \frac{0.059}{2} \log\left(\frac{\overset{\nearrow 1.9 \times 10^{-13}}{K_{sp}}}{10^{-8} \times 0.19}\right)$$

$$\boxed{E = 1.638V}$$

Q.31 The overall formation constant for the reaction of 6 mol of CN^- with cobalt(II) is 1×10^{19}. The standard reduction potential for the reaction

$[Co(CN)_6]^{3-} + e^- \rightarrow Co(CN)_6^{4-}$ is -0.83 V.

Calculate the formation constant of $[Co(CN)_6]^{3-}$

Given $Co^{3+} + e^- \rightarrow Co^{2+}$; E° = 1.82 V

① $Co^{2+} + 6CN^- \rightleftharpoons [Co(CN)_6]^{4-}$ $K_{f_1} = 10^{19}$

② $[Co(CN)_6]^{3-} + 1e^- \rightleftharpoons [Co(CN)_6]^{4-}$ $E^\circ = -0.83$

$$E^\circ = \frac{0.059}{1} \log K_2$$

$$K_2 = 8.55 \times 10^{-15}$$

③ $Co^{3+} + 1e^- \rightarrow Co^{2+}$ $E^\circ = 1.82$

$$E^\circ = \frac{0.059}{1} \log K_3$$

$$K_3 = 7.02 \times 10^{30}$$

④ $Co^{3+} + 6CN^- \rightleftharpoons [Co(CN)_6]^{3-}$

④ = ③ − ② + ①

$\therefore K_4 = \underline{K_3 \times K_1} = \underline{(7.03 \times 10^{30}) \times 10^{19}}$

~~Calculations~~

$$\frac{m}{E} = \frac{It}{96500}$$

$$E = \frac{m \times 96500}{It}$$

(Q.32) The voltage of the cell

Zn(s) | $Zn(CN)_4^{2-}$(0.450M), CN^-(2.65×10^{-3}M) || Zn^{2+}(3.84×10^{-4} M) | Zn(s)

is E = + 0.099 V. Calculate the constant K_f for $Zn^{2+} + 4CN^- ⇌ Zn(CN)_4^{2-}$, the only Zn^{2+} + CN complexation of importance.

Anode: $Zn \rightleftharpoons \underset{(C_1)}{Zn^{2+}} + 2e^-$

~~or~~

~~$Zn + 4CN^- \rightleftharpoons [Zn(CN)_4]^{2-} + 2e^-$~~

Cathode: $Zn^{2+} + 2e^- \longrightarrow \underset{(s)}{Zn}$

(C_2)

3.84×10^{-4}

$$\underset{(C_1)}{Zn^{2+}} + 4CN^- \rightleftharpoons [Zn(CN)_4]^{2-} \quad K_f$$

$$K_f = \frac{[Zn(CN)_4]^{2-}}{[CN^-]^4 \times C_1}$$

$$\therefore C_1 = \frac{(0.45)}{(2.65 \times 10^{-3})^4 \times K_f}$$

Cell eqn: $Zn + Zn^{2+} \rightleftharpoons Zn^{2+} + Zn$

$Q = \frac{c_1}{c_2}$, $n = 2$, $E^\circ_{cell} = 0$
∵ Conc^n cell

$$\therefore \quad E_{cell} = \cancel{E^\circ_{cell}}^{\,0} - \frac{0.059}{2}\log\frac{c_1}{c_2}$$

$$\therefore \quad \frac{0.099 \times 2}{0.059} = \log\frac{c_2}{c_1}$$

$$3.35 = \log\frac{c_2}{c_1}$$

$$2238.7 = \frac{c_2}{c_1} \qquad \frac{3.84\times10^{-4}}{(0.45)\times(2.65\times10^{-3})^4\times K_f}$$

$$\boxed{K_f = 5.32 \times 10^{16}}$$

$$C_1 = 1.692 \times 10^{-7}$$

$$K_f = \frac{[Zn(CN)_4^{2-}]}{[Zn^{2+}][CN^-]^4}$$

$$= 5.39 \times 10^{16}$$

Check Ans !!

Q. 33 The voltage of the cell

Pt | H_2(g, 608torr) | HClO (4.34×10^{-3}M) || S.C.E. is E = + 0.532V. Calculae the dissociation constant for HClO. Given, E(SCE) = 0.242.

A:

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$\left(\frac{608}{760}\right)$$

~~$\sqrt{K_a \times 4.34 \times 10^{-3}}$~~

$$E_A = \underset{\downarrow\atop 0}{E^\circ} - \frac{0.059}{2} \log \frac{[H^+]^2}{\left(\frac{608}{760}\right)}$$

$$0.532 = \underset{\downarrow\atop 0.242}{E_{SCE}} + E_A$$

$$E_A = 0.29 = -0.059 \log \frac{\left(K_a \times 4.34 \times 10^{-3}\right)}{\left(\frac{608}{760}\right)}$$

$$\boxed{K_a = 2.24 \times 10^{-3}}$$

$$0.29 = -\frac{0.059}{2} \log \frac{[H^+]^2}{\frac{608}{760}}$$

$$[H^+] = 1.0872 \times 10^{-5}$$

Answer Correction Check for ΔS^o

Check !!

(34) Q. At 27°C, $\left(\frac{\partial E^o}{\partial T}\right)_p = -1.25 \times 10^{-3}\ VK^{-1}$ and $E^o = 1.36$ V for the cell

$Pt|H_2(g)||\ HCl(aq)|Cl_2|Pt$ $\quad H_2, H^+ \| Cl_2, Cl^-$

Calculate entropy and enthalpy change in their standard state.

$$dG = VdP - SdT$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \Rightarrow \Delta S = \left(\frac{-\partial \Delta G}{\partial T}\right)_p$$

$$\Delta S = +nF\left(\frac{\partial E}{\partial T}\right)_p = +2 \times 96500(-1.25 \times 10^{-3}) = \boxed{-241.25\ JK^{-1}}$$

~~Cell eqn: $H_2 + Cl^- \rightarrow H^+$~~

$$\Delta G = -nF(1.36) = -2 \times 96500 \times 1.36 = -262,480\ J$$

$$\Delta G = \Delta H - \underset{(300)}{T}(\Delta S)$$

$$\therefore \Delta H = -262480 + 300(-241.25)$$

$$\boxed{\Delta H = -334.85\ kJ}$$

Q.35 How long a current of 2A has to be passed throuh a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with 5 μm thick layer? Density of silver = 10.8 g/cm^3.

$$Ag^+ + 1e^- \rightarrow Ag$$

Mass of Ag deposited $= (80 \times 5 \times 10^{-4})\,cm^3 \times 10.8\ g/cm^3$

$= \cancel{4.32\,gm}\ 0.432\,gm$

Faraday's 1st law:

$$\therefore 0.432 = \frac{108 \times (2 \times t)}{1 \times 96500}$$

$$\boxed{t = 193\cancel{0}\ sec}$$

Answer correction !!

Q.36 3A current was passed thorough an aqueous solution of an unknown salt of Pd for 160 min 50 sec. 5.32 gm of Pd^{+n} was deposited at cathode. Find n. (Atomic wt. of Pd = 106.4)

$$Pd^{n+} + ne^- \rightleftharpoons Pd$$

Faraday's 1st law.

$$5.32 = \frac{106.4 \times (3 \times 9650)}{n \times 96500}$$

$$\boxed{n = 6}$$

Q.37 A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95 g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from $CuSO_4$?

$$M^{2+} + 2e^- \rightarrow M$$

1st Law (Faraday)

$$1.95 = \frac{(Mwt) \times 10 \times 330}{2 \times 96500}$$

$$\boxed{(Mwt)_M = 114.04 \text{ gm}}$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$1.95 = \frac{63.5 \times Q}{2 \times 96500}$$

~~Q = 5763.39 Coloumb~~

$$\boxed{Q = 5926.77 \text{ Coloumbs}}$$

Q.33 50 mL of 0.1 M $CuSO_4$ solution is electrolyzed with a current of 0.965 A for a period of 200 sec. The reactions at electrodes are:

Cathode : $Cu^{2+} + 2e^- ⍰ Cu(s)$ Anode : $2H_2O ⍰ O_2 + 4H^+ + 4e$.

Assuming no change in volume during electrolysis, calculate the molar concentration of Cu^{2+}, H^+ and SO_4^{2-} at the end of electrolysis.

$[SO_4^{2-}]$ will remain same, i.e. $\boxed{0.1 M}$
(∵ it is not affected due to electrolysis)

Faraday's 1st law:

$$n_{Cu^{2+}} \text{ deposited} = \frac{0.965 \times 200}{96500 \times 2} = 10^{-3} \text{ moles}$$

$\{ Cu^{2+} + 2e^- \longrightarrow Cu, \therefore n\text{-}f = 2 \}$

$$\therefore [Cu^{2+}]_{\text{at end}} = \frac{\left(\frac{50}{1000} \times 0.1 - 10^{-3} \right)}{\frac{50}{1000}} = 0.08 M$$

$$\boxed{\therefore [Cu^{2+}]_{@ \text{ end}} = 0.08 M}$$

$$(n_{O_2})_{\text{formed}} = \frac{0.965 \times 200}{96500 \times 4} = 5 \times 10^{-4}$$

$(\because n.f. \text{ of } O_2 = 4)$

$$[H^+]_{end} = \frac{2\times10^{-3}}{50/1000}$$

$$\boxed{[H^+]_{end} = 0{\cdot}04\ M}$$

~~Calculation~~

Q. 39 10 g fairly concentrated solution of $CuSO_4$ is electrolyzed using 0.01 F of electricity. Calculate :

(a) The weight of resulting solution (b) Equivalent of acid or alkali in the solution.

$[SO_4^{2-}]$ is not affected.

$wt_{O_2} = 0.01 \times \frac{32}{4}$

$= 0.08$ g

$Cu^{2+} + 2e^- \rightarrow Cu$

∴ Wt of Cu deposited. $= \frac{\cancel{63.5}\ 63.5 \times 0.01 \cancel{F}}{2 \times \cancel{96500}}$

$= 0$ ~~.32 gm~~ 0.3175 g.

∴ Wt of resulting solution = ~~10 − 0.32~~

= ~~9.67 gm~~

$= 10 - 0.3175 - 0.08 = 9.6025$ g

b) Eq. of Acid = Eq. of Alkali = (Eq. of salt deposited)

0.01 F of electricity corresponds to 0.01 Eq.

∴ $\boxed{\text{Eq of Acid} = \text{Eq. of Alkali} = 0.01\ \text{Eq}}$

Q.40 An electric current is passed through electrolytic cells in series one containing $Ag(NO_3)(aq)$. and other $H_2SO_4(aq)$. What volume of O_2 measured at 27°C, 1 atm and 750 mm^3 Hg pressure would be liberated from H_2SO_4 if

(a) one mole of Ag^+ is deposited from $AgNO_3$ solution

(b) 8×10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution. $\left(R = \frac{1}{12} 11 \text{ atm}, N_a = 6 \times 10^{23}\right)$

Cathode:

$$Ag^+ + 1e^- \rightarrow Ag$$

Faraday's 1st law

$$n_{Ag} = \frac{Q}{96500 \times 1}$$

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Faraday's 1st law

$$n_{O_2} = \frac{Q}{4 \times 96500}$$

$$\downarrow$$

$$\frac{\left(\frac{750}{760}\right) V}{(0.0821) \times 300}$$

A) $$n_{Ag} = 1 = \frac{Q}{96500 \times 1} \Rightarrow Q = 96500$$

$$\therefore \frac{750 \times V}{760 \times \frac{1}{12} \times 300} = \frac{\cancel{96500}\ 1}{4 \times \cancel{96500}}$$

$\boxed{~~V = 6.24 L~~}$ $V = 6.33L$.

B) $$n_{Ag} = \frac{8 \times 10^{22}}{6 \times 10^{23}} = \frac{Q}{96500}$$

$$\therefore Q = 96500 \times \frac{8}{6 \times 10}$$

$\therefore \boxed{V = ~~0.83~~ L}$ 0.844

Q. 41 Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a currecnt of 5A be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2gm Hg (Cd=112.4).

$$Cd^{2+} + 2e^- \rightarrow Cd.$$

12% Cd-Hg ⇒ 12 gm Cd combines with 88 gm Hg

12 gm Cd → 88 gm Hg

$\therefore$ 1 gm Hg ⇒ $\frac{12}{88}$ gm Cd

$\therefore$ 2 gm Hg ⇒ $2 \times \frac{12}{88}$ gm Cd

(Faraday's 1st law for Cd)

$$\therefore \quad 2 \times \frac{12}{88} = \frac{112.4 \times (5 \times t)}{2 \times 96500}$$

$$\boxed{t = 93.66 \text{ sec}}$$

Q. ⑷② After electrolysis of NaCl solution with inert electrodes for a certanin period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltammeter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.

~~At~~ Cathode:

$$2H^+ + 2e^- \rightarrow H_2$$

or

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

(Electrolysis of aq. NaCl)

Faraday's 1st law

$$n_{H_2} = \frac{Q}{2 \times 96500}$$

(Q is same, ∵ they are connected in series)

$$\therefore n_{H_2} = \frac{\cancel{96500}}{2 \times \cancel{96500}}$$

$= 0.5$ moles

~~At~~ Cathode:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

(Electrolysis of Cu^{2+})

$\downarrow$

Faraday's 1st law

$$31.75 = \frac{63.5 \times Q}{2 \times 96500}$$

$$Q = 96500$$

$$2H_2O + 2e^- \longrightarrow \underset{\substack{\downarrow \\ 0.5\text{ mole}}}{H_2} + \underset{\substack{\downarrow \\ 1\text{ mole}}}{2OH^-}$$

∴ ~~$[OH^-] = \frac{1}{\frac{600}{1000}} = 1.66$ M or 1.66 N~~

Q. 43 Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x liberated is 0.54g and the iodine is completely reduced by 50 cc of 0.1 M sodium thiosulphate. Find the equivalent mass of x.

At Anode:

$$I^- \rightarrow \frac{1}{2} I_2 + 1e^-$$

At Cathode:

$$M^{x+} + xe^- \rightarrow M$$

FARADAY's 1st Law.

$$0.54 = \underbrace{\left(\frac{(Mwt_M)}{x}\right)}_{(Eq\ wt)_M} \times \frac{Q}{96500} \quad ①$$

(For Metal M)

$$Wt\ of\ I_2 = \frac{(Mwt)_{I_2} \times Q}{2 \times 96500}$$

$$(Mol\ of\ I_2) = \frac{Q}{2 \times 96500} \quad ②$$

(For ~~Metal~~ I_2)

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

$Na_2S_2O_3$: $(50 \times 0.1 \times 10^{-3})$ moles

I_2: $25 \times 0.1 \times 10^{-3}$ moles

$$0.54 = (Eq\ wt)_M \times \frac{(2 \times \cancel{96500}) \times (25 \times 0.1 \times 10^{-3})}{\cancel{96500}}$$

$$\frac{0{\cdot}54}{E} = \frac{50}{1000} \times 0{\cdot}1 \times 1$$

$$E = 108$$

Q.44 The standard reduction potential values, E°(Bi^{3+}|Bi) and E°(Cu^{2+} | Cu) are 0.226 V and 0.344 V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. to what value can [Cu^{2+}] be brought down before bismuth starts to deposit, in electrolysis.

$E^{0}_{Bi^{3+}/Bi} = 0.226\ V$ | $E^{0}_{Cu^{2+}/Cu} = 0.344\ V$

Initially SRP of Cu^{2+} > SRP of Bi^{3+}

∴ Cu^{2+} will get reduced.

$Cu^{2+} + 2e^- \rightarrow Cu$

$$E_{Cu^{2+}/Cu} = E^{0}_{Cu^{2+}/Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]} \quad \left\{ \text{Nernst eqn} \right\}$$

Eventually, when E of this cell will be equal to $E^{0}_{Bi^{3+}/Bi}$ as $[Cu^{2+}] \downarrow$. At this point, Bismuth will start to deposit

i.e.

$$E^{0}_{Bi^{3+}/Bi} = E_{Cu^{2+}/Cu} = E^{0}_{Cu^{2+}/Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$0.226 = 0.344 + \frac{0.059}{2} \log [Cu^{2+}]$$

$$\boxed{[Cu^{2+}] = 10^{-4} M}$$

Q.45 A current of 2amps is used for 60 min. to electrolyze copper from a solution of Cu^{2+} at a potential of 0.337 volts.

(a) How many coulombs are used

(b) How many moles Cu(s) are plated out?

(c) What weight Cu(s) in grams is plated out?

(d) What power in watts was used?

a) $Q = i \times t = 2 \times 60 \times 60 = \boxed{7200 \text{ Columbs}}$

Faraday's 1st law:

$$(\text{Wt Cu})_{\text{deposited}} = \frac{(\text{Mwt})_{\text{Cu}}}{2 \times 96500} \times 7200$$

~~(Moles of Cu) deposited~~

$Cu^{2+} + 2e^- \rightarrow Cu$ $(n\text{-}f = 2)$

c) $(\text{Wt Cu})_{\text{deposited}} = \boxed{2.036 \text{ gm}}$

b) Moles of (Cu) deposited $= \boxed{0.037 \text{ moles}}$

d) Power $= V \times i \times t$

$= 0.337 \times 2$

$= \boxed{0.67 \text{W}}$

Q. 46 If you electrolyze a solution of Ni^{2+} (aq) to form Ni(s) for 2.00 h using a current of 2.50 amp, what mass of Ni(s) (AW = 58.69 g/mol) is produced at the cathode?

$$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$$

Faraday's 1st law

$$(Wt)_{Ni} = \frac{58.69 \times (2 \times 3600 \times 2.5)}{2 \times 96500}$$

$$\boxed{(Wt)_{Ni} = 5.47 \text{ gm}}$$

Q. 47 A battery was used to supply a constant current of what was believed to be exactly 0.45 A as read on a meter in the external circuit. The cell was based on the electrolysis of a copper sulphate solution. During the 30 min, that current was allowed to flow, a total of 0.3 g of copper metal was deposited at the cathode. Determine the extent to which the meter was inaccurate

$Cu^{2+} + 2e^- \rightarrow Cu$

Faraday's 1st law

$$W = Z \times Q$$

$$\therefore \quad 0.3 = \frac{63.5\,(i \times 30 \times 60)}{2 \times 96500}$$

$$i = 0.506\,A$$

~~∴ % inaccuracy = (0.506 − 0.45)/0.506 × 100~~

$$\% \text{ inaccuracy} = \frac{(0.506 - 0.45)}{0.506} \times 100$$

$$= \boxed{11.06\,\%}$$

(Check → If payload is to be used then ρ_{air} & ρ_{H_2} must be given)

Q-48 Q. A balloon is being filled with hydrogen produced by the electrolysis of an aqueous solution of an acid. How long will it take to generate enough hydrogen to lift 1.5 kg by using a current of 8.5 A?

$$2H^+ + 2e^- \rightarrow H_2$$

~~$10^3 \times 1.5 = \frac{\cancel{2} \times (8.5 \times t)}{\cancel{2} \times 96500}$~~

~~$t = 17029.41$ sec~~

~~$t = 17,029,411.76$ sec or 4730 hrs~~

$$1500 = V\left(\frac{P \times 29}{RT} - \frac{P \times 2}{RT}\right)$$

$$n_{H_2} = \frac{1500}{27}$$

$$\frac{1500}{27} \times 2 = \frac{8.5 \times t}{96500}$$

$t = 350.4$ hours.

Q.49 A current of 3.7 A is passed for 6 hrs. between Ni electrodes in 0.5L of 2M solution of $Ni(NO_3)_2$. What is the molarity of solution at the end of electrolysis?

C : $Ni^{2+} + 2e^- \rightarrow Ni$

~~$(Wt_{Ni})_{deposited} = \frac{(Mwt)_{Ni}}{\boxed{2} \times 96500} \times (Q)$~~ ~~(By Faraday's 1st law)~~

~~$\underset{n\text{-}f}{\boxed{2}}$; $Q \downarrow i \times t \downarrow 3.7 \times 6 \times 3600$~~

~~$\therefore (\text{moles of } Ni)_{deposited} = \frac{3.7 \times 6 \times 3600}{2 \times 96500}$~~

~~$= 0.41$ moles~~

~~Molarity @ end of electrolysis of $[Ni^{2+}]$~~

~~$= \frac{\text{initial moles} - \text{final moles}}{\text{Volume}}$~~

~~$= \frac{0.5 \times 2 - 0.41}{0.5} = \boxed{1.18 M}$~~

$[NO_3^-]$ will remain as 2M (same)

@ A : $Ni \rightleftharpoons Ni^{2+} + 2e^-$

Ni is deposited but @ the same time it will be electrolysed also

Q-50 Q. The resistance of a conductivity cell filled with 0.01N solution of NaCl is 210 ohm at18°C.Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm?1) cm^{-1}

$$R = \rho\left(\frac{L}{A}\right)$$

$$210 = \rho(0.88)$$

$$\rho = \frac{210}{0.88} \text{ ohm cm}$$

$$\therefore \quad k = \frac{1}{\rho} = 4.19 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$$

$$\Lambda_E = \frac{k \times 1000}{N} = \frac{4.19 \times \overset{1}{\cancel{10^{-3}}} \times \cancel{1000}}{0.01}$$

$$\boxed{\Lambda_E = 419 \text{ mho cm}^2 \text{ eq}^{-1}}$$

Check

Q.57 ~~Q.~~ The molar conductivity of 0.1 M CH_3COOH solution is 4.6 S cm^2 mole^{-1}. What is the specific conductivity and resistivity of the solution ?

$$\Lambda_M = \frac{K \times 1000}{M} \quad \Bigg| \quad \Lambda_E = \frac{K \times 1000}{N}$$

K → specific conductivity

M → Molarity   N → Normality

$$N = m \times (n.f)$$

$$\therefore \Lambda_E = \frac{\Lambda_m}{(n.f)} \rightarrow \text{n factor}$$

For CH_3COOH, $n.f = 1$

$$\rightarrow \Lambda_E = \frac{\Lambda_M}{1}$$

$$\frac{K \times 1000}{0.1} = 4.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\boxed{K = 4.6 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}}$$

$$\boxed{\text{Resitivity} = \frac{1}{K} = 2.173 \times 10^{3} \text{ ohm cm}}$$

(Check Ans for ii)

Q.52 Q. The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm^2 and 2 cm apart is $8 \times 10^{⍰7}$ S cm$^{⍰1}$. 8×10^{-7} S cm^{-1}

(i) What is resistance of conductivity cell ?

(ii) What current would flow through the cell under an applied potential difference of 1 volt?

(i) $$R = \rho\left(\frac{L}{A}\right)$$

$$\sigma = 8 \times 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1} \therefore \rho = \frac{1}{\sigma} = \frac{10^7}{8} \text{ ohm cm}$$

$$\therefore R = \frac{10^7}{8}\left(\frac{2}{4}\right)$$

$$\boxed{R = 6.25 \times 10^5 \text{ ohm}}$$

(ii) $$V = iR$$

$$1 = i \times (6.25 \times 10^5)$$

$$\boxed{i = 1.6 \times 10^{-6} \text{ A}}$$

Q.53 Q. Resistivity of 0.1M KCl solution is 213 ohm cm in a conductivity cell. Calculate the cell constant if its resistance is 330 ohm.

$$R = \rho \overbrace{\left(\frac{L}{A}\right)}^{\text{cell constant}}$$

$$330 = (213)\left(\frac{L}{A}\right)$$

$$\boxed{\therefore \text{ cell constant} = 1.549\ \text{cm}^{-1}}$$

Q.54 a. Resistance of a 0.1M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1M KCl is 1.29×10^{-2} ohm^{-1} cm^{-1}. The resistance of 0.1M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1M NaCl solution.

For KCl

$$R_1 = \rho_1 \left(\frac{L}{A}\right)$$

For NaCl

$$R_2 = \rho_2 \left(\frac{L}{A}\right)$$

(Cell constant will remain same)

$$300 = \frac{1}{k_1}\left(\frac{L}{A}\right)$$

$$\left(\frac{L}{A}\right) = 300 \times k_1$$

$$\therefore R_2 = \frac{1}{k_2}(300 \times k_1)$$

$$k_2 = \frac{300 k_1}{R_2}$$

$$\boxed{k_2 = 1.0184 \times 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}}$$

$$\boxed{\Lambda_E = \frac{k_2 \times 1000}{0.1} = 10184 \text{ hm}^{-1}\text{cm}^{2}\text{eq}^{-1}}$$

Check for Ans

ohm

(Q.55) ~~a~~. For 0.01N KCl, the resistivity 709.22 mho cm. Calculate the conductivity and equivalent conductance.

$$(K)\ \text{Conductivity} = \frac{1}{\text{Resitivity}\ (\rho)}$$

$$K = \frac{1}{709.22}\ \text{mho cm}^{-1}$$

$$\boxed{K = 0.00141\ \text{ohm}^{-1}\ \text{cm}^{-1}}$$

$$\text{Specific conductance} = K\left(\frac{A}{L}\right)$$

~~taken~~ Conductance of a solⁿ of 1cc ~~containing~~ in which distance b/w plates is 1cm

$$\boxed{\therefore K = 0.00141\ \text{ohm}^{-1}\ \text{cm}^{-1}}$$

$$\text{Equivalent conductance } \Lambda_E = \frac{K \times 1000}{N}$$

$$= \frac{0.00141 \times 1000}{0.01}$$

$$= \boxed{141\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}}$$

~~Rough~~

~~$R = \rho \frac{(L)}{(A)}$~~

~~$\rho =$ ohm cm~~

$\rho = 709.22$ ohm cm

$= 7.0922$ ohm m

$K = \frac{1}{\rho} = 0.141$ ohm^{-1} m^{-1}

$$\Lambda_e = \frac{0.141 \times 1}{1000 \times 0.01}$$

$=$ ~~0.0014~~ 0.0141 ohm^{-1} m^{2} eq^{-1}

(At wt Ba = 137.3)

Q.56 ~~Q.~~ A solution containing 2.08 g of anhydrous barium chloride is 400 CC of water has a specific conductivity 0.0058 ohm^{-1}cm^{-1}. What are molar and equivalent conductivities of this solution.

$$[BaCl_2] = \left[\frac{2.08}{(137.3+2\times 35.5)}\right] \Big/ 0.4 = 0.024\,M$$

$$\Lambda_M = \frac{K\times 1000}{0.024} = \frac{0.0058\times 1000}{0.024}$$

$$\boxed{\Lambda_M = 232.33\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}}$$

$$0.024\,M \times \underset{\substack{\downarrow \\ n\text{-}f =}}{2} = 0.048\,N$$

$$\therefore \boxed{\Lambda_E = \frac{K\times 1000}{0.048} = 116.16\,\text{ohm}^{-1}\,\text{cm}^2\,\text{eq}^{-1}}$$

Q:57 Q. Equivalent conductance of 0.01 N Na_2SO_4 solution is 112.4 ohm^{-1} cm^2 eq^{-1}. The equivalent conductance at infinite dilution is 129.9 ohm^{-1} cm^2. What is the degree of dissociation in 0.01 N Na_2SO_4 solution?

$$\alpha = \frac{\Lambda_{Na_2SO_4} \rightarrow 112.4}{\Lambda^0_{Na_2SO_4} \rightarrow 129.9} = 0.8652$$

$$\boxed{\alpha = 86.52\,\%}$$

~~Check Ans!!~~

Q.58

Q. Specific conductance of a saturated solution of AgBr is 8.486×10^{-7} $ohm^{-1}cm^{-1}$ at 25^0C. Specific conductance of pure water at 25°C is 0.75×10^{-6} ohm^{-1} cm^{-2} Λ^∞_m For KBr , $AgNO_3$ and KNO_3 are 137.4 , 133 , 131 (S cm^2 mol^{-1}) respectively. Calculate the solubility of AgBr in gm/litre.

$\because$ AgBr is a sparingly soluble salt

$\therefore$ $\Lambda_{AgBr} = \Lambda^\infty_{AgBr}$

$\frac{1000 \times K_{AgBr(s)}}{S}$

(By Kohlrausch law)

$\left(\Lambda^\infty_{KBr} + \Lambda^\infty_{AgNO_3} - \Lambda^\infty_{KNO_3}\right)$

$= 139.4$ ohm^{-1} cm^2 mol^{-1}

$$K_{AgBr(s)} = K_{AgBr(aq)} - K_{H_2O} = (8.486\times10^{-7} - 7.5\times10^{-7}) \ ohm^{-1}cm^{-1}$$

$$= 0.986\times10^{-7} \ ohm^{-1}cm^{-1}$$

$$\therefore \frac{1000 \times 0.986\times10^{-7}}{S} = 139.4$$

$$\boxed{S = 7.07 \times10^{-7} \ mol/L}$$

$= 1.33\times10^{-4}$ g/L.

~~Calculation~~

Q. 59 Saturated solution of AgCl at 25°C has specific conductance of 1.12×10^{-6} ohm^{-1} cm^{-1}. The λ_e^∞ Ag$^+$ and λ_e^∞Cl$^-$ are 54.3 and 65.5 ohm^{-1} cm^2 / equi. respectively. Calculate the solubility product of AgCl at 25°C.

As AgCl is a ppt.,
∴ for sparingly soluble salts

$$\Lambda_{AgCl} \quad \Lambda^0_{AgCl}$$

$$\frac{K_{AgCl}\times 1000}{S} \qquad (\lambda^0_{Ag^+} + \lambda^0_{Cl^-})$$

$$AgCl_{(s)} \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{Cl^-} \qquad S^2 = K_{sp}$$

$$\therefore S = \sqrt{K_{sp}}$$

$$\frac{1.12\times10^{-6}\times1000}{\sqrt{K_{sp}}} = 54.3 + 65.5$$

$$\boxed{K_{sp} = 8.74\times10^{-11}\ \text{mol}^2 L^{-2}}$$

Q. (60) Hydrofluoric acid is weak acid. At 25°C, the molar conductivity of 0.002M HF is 176.2 ohm^{-1} cm^{2} mole^{-1}. If its Λ_m^∞ = 405.2 ohm^{-1} cm^{2} mole^{-1}, calculate its degree of dissociation and equilibrium constant at the given concentration.

$$\alpha = \frac{\Lambda}{\Lambda^\infty} = \frac{176.2}{405.2} = 0.4348$$

or $\boxed{\alpha = 43.48\%}$

$$\begin{array}{ccccc} HF & \rightleftharpoons & H^+ & + & F^- \\ c & & 0 & & 0 \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

$$K_a = \frac{(c\alpha)(\cancel{c}\alpha)}{\cancel{c}(1-\alpha)}$$

$$\therefore \quad K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$\boxed{K_a = 6.68 \times 10^{-4}}$$

Q.61 The value of Λ_m^∞ for HCl, NaCl and CH_3CO_2Na are 426.1, 126.5 and 91 S cm^2 mol^{-1} respectively. Calculate the value of Λ_m^∞ for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at 25° C, calculate its degree of dissociation.

$$\alpha = \frac{\Lambda}{\Lambda^\infty}$$

For calculation of Λ°, using Kohlrausch's law:

$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COO^-} + \Lambda^\infty_{H^+}$ —④

Given:

$\Lambda^\infty_{HCl} = \Lambda^\circ_{H^+} + \Lambda^\circ_{Cl^-} = 426.1$ —①

$\Lambda^\infty_{NaCl} = \Lambda^\circ_{Na^+} + \Lambda^\circ_{Cl^-} = 126.5$ —②

$\Lambda^\circ_{CH_3COONa} = \Lambda^\infty_{CH_3COO^-} + \Lambda^\infty_{Na^+} = 91$ —③

④ = ① − ② + ③

$$\therefore \boxed{\Lambda^\infty_{CH_3COOH} = 426.1 - 126.5 + 91 = 390.6 \text{ cm}^2\text{mol}^{-1}}$$

$$\alpha = \frac{\Lambda = 48.15}{\Lambda^\infty = 390.6} = 0.1237$$

$$\text{or } \boxed{\alpha = 12.32\ \%}$$

Q.62. Calculate the specific conductance of a 0.1 M aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and 6.80×10^{-8} $m^2\ v^{-1}\ s^{-1}$, respectively.

$$\frac{\Lambda_{Na^+}}{96500} = u_{Na^+} \quad \& \quad u_{Cl^-} = \frac{\Lambda_{Cl^-}}{96500}$$

$$\Lambda_{Na^+} = 4.11\times10^{-3}, \quad \Lambda_{Cl^-} = 6.56\times10^{-3}$$

$$\Lambda_{NaCl} = 1.067\times10^{-2}\ ohm^{-1}\ m^2\ mol^{-1}$$

~~$\therefore \Lambda_{NaCl} = 1.067\times10^{2}\ ohm^{-1}\ cm^2\ mol^{-1}$~~

~~$\therefore \frac{K\times1000}{0.1} = 1.067\times10^{2}$~~

~~$K = 106.7\ ohm^{-1}\ cm^{-1}$~~

$$K = \Lambda_{NaCl}\times1000\times0.1$$

$$= 1.067\ ohm^{-1}\ m^{-1}$$

Q. 63 For the strong electroytes NaOH, NaCl and $BaCl_2$ the molar ionic conductivities at infinite dilution are 248.1×10^{-4}, 126.5×10^{-4} and 280.0×10^{-4} mho cm^2 mol^{-1} respectively. Calculate the molar conductivity of $Ba(OH)_2$ at infinite dilution.

Using Kohlrausch's law

$$\Lambda^{\infty}_{NaOH} = \Lambda^{\infty}_{Na^+} + \Lambda^{\infty}_{OH^-} = 248.1\times10^{-4} \quad -①$$

$$\Lambda^{\infty}_{NaCl} = \Lambda^{\infty}_{Na^+} + \Lambda^{\infty}_{Cl^-} = 126.5\times10^{-4} \quad -②$$

$$\Lambda^{\infty}_{BaCl_2} = \Lambda^{\infty}_{Ba^{2+}} + 2\Lambda^{\infty}_{Cl^-} = 280\times10^{-4} \quad -③$$

$$\Lambda^{\infty}_{Ba(OH)_2} = \Lambda^{\infty}_{Ba^{2+}} + 2\Lambda^{\infty}_{OH^-} \quad -④$$

④ = ③ + 2① − 2②

$$= 280\times10^{-4} + 2\times248.1\times10^{-4} - 2(126.5\times10^{-4}$$

$$= (280 + 496.2 - 253.0)\times10^{-4}$$

$$= \boxed{523.2\times10^{-4}}$$

mho cm^2 mol^{-1}

Check for Answer !!

Q.64 At 25°C, $\lambda_m^\infty(H^+) = 3.4982 \times 10^{-2}$ S m^2 mol^{-1} and $\lambda_m^\infty(OH^-) = 1.98 \times 10^{-2}$ S $m^2 mol^{-1}$.

Given: Sp. conductance = 5.1×10^{-6} S m^{-1} for H_2O, determine pH and K_W.

~~$K = [H^+]\lambda_{H^+} + [OH^-]\lambda_{OH^-}$~~

~~$[H^+] = [OH^-] = \sqrt{K_w}$~~

~~$K = [\sqrt{K_w}][\lambda_{H^+} + \lambda_{OH^-}]$~~

~~∵ H_2O is a weak electrolyte~~

~~∴ $\lambda_{H^+} = \lambda^\infty_{H^+}$ & $\lambda_{OH^-} = \lambda^\infty_{OH^-}$~~

~~∴ $\lambda^\infty_{H^+} + \lambda^\infty_{OH^-} = \lambda^\infty_{H_2O}$ (Kohlrausch's law)~~

~~$$\therefore K_w = \left(\frac{\overset{5.1\times10^{-8}}{K}}{\underset{5.4782\times10^{-2}}{\Lambda^\infty_{H_2O}}}\right)^2$$~~

~~$$\alpha = \frac{\Lambda_{H_2O}}{\Lambda^\infty_{H_2O}} = \frac{\left(\frac{5.1\times10^{-8}\times1000}{55.5}\right)}{(547.82)} = 1.67\times10^{-9}$$~~

$c\alpha = [H^+] = 9.2 \times 10^{-8}$ | $K_w = [H^+][OH^-]$

$$\Lambda^{\infty} = 3.4982\times10^{-2} + 1.498\times10^{-2}$$

$$= 4.9962\times10^{-2}$$

$$4.9962\times10^{-2} = 5.1\times10^{-6} \times \frac{1}{1000[H^+]}$$

$$\Rightarrow [H^+] = 1.0208\times10^{-7}$$

$$pH = 6.99$$

$$K_w = 1.042\times10^{-14}$$